197

CELLULOSE RESEARCH

A Symposium

COUNCIL OF SCIENTIFIC
& INDUSTRIAL RESEARCH
NEW DELHI

CELLULOSE RESEARCH

A SYMPOSIUM HELD UNDER THE AUSPICES
OF THE CELLULOSE RESEARCH COMMITTEE
AT ATIRA, AHMEDABAD (February 4–6, 1957)

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PREFACE

Industries based on cellulosic raw materials play a very important part in India's economy. Cotton and jute textiles, paper, pulp and rayon are the largest and the most important amongst these. It has been estimated that they contribute an annual income of about a thousand crores of rupees to the country. Recognizing the value of specialized research which could improve the utilization of cellulosic raw materials, the efficiency of processing industry, and the quality of end-products, the Council of Scientific & Industrial Research (CSIR) constituted the Cellulose Research Committee in 1940.

The Cellulose Research Committee has been in existence for the past seventeen years. In order to play a significant role it feels that its activities have to be directed along two principal directions: The first relates to the stimulation of interest in fields of cellulose research which are likely to contribute to the understanding of basic problems in cellulose chemistry and the industrial application of the knowledge that is so derived; the second deals with financial support to worthwhile research schemes sponsored by active research workers in government and private research institutions, universities and industries. To fulfil the first aim, the Committee decided to hold an annual symposium on cellulose with the following objectives: (i) to review the current status of knowledge in important branches of the subject which come within the purview of the Committee and (ii) to afford an opportunity for active research workers to present the results of their investigations. It is hoped that the symposium would stimulate the undertaking of original projects directed to the real needs of the country.

The first annual symposium was held from Feb. 4–6, 1957 at Ahmedabad at the generous invitation of the Ahmedabad Textile Industry's Research Association. The symposium was divided into five half-day sessions and 19 papers were presented. These dealt with chemistry of cellulose, structure and mechanical properties of cellulose, reactions of cellulose with cross linking agents, cellulose for the rayon industry and problems of jute, paper and pulp industries. There was a very lively discussion in each session.

In presenting this volume of collected contributions made at the symposium, I wish to thank on behalf of the Cellulose Research Committee, Dr. P. C. Mehta, Assistant Director, ATIRA, who acted as the Organizing Secretary for the symposium and to the CSIR for undertaking the publication of the proceedings of the symposium.

VIKRAM A. SARABHAI
Chairman
Cellulose Research Committee

Ahmedabad
Oct. 4, 1957

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Cellulose Research in India

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The progress of cellulose research in India, with particular reference to researches sponsored by the CSIR Cellulose Research Committee, has been briefly reviewed and suggestions have been made for the promotion of research in certain defined fields. The present position of cellulose industries in India and possibilities for their development have been discussed. Researches on cellulose in Europe and America have been briefly referred to.

This symposium provides a good opportunity to review the progress of cellulose research in India, with emphasis on the contributions made towards the fundamental and applied knowledge of the subject. The history of this research can be broadly divided into two periods, namely, the first quarter of this century and the period subsequent thereto.

A survey of raw materials for the paper industry was initiated in the early years of the century, following the foundation of the Forest Research Institute at Dehra Dun in 1906. Raitt's work[1] on cellulosic raw materials, particularly bamboo, provided valuable information, and to him and his colleagues and successors, the paper industry of this country owes a heavy debt. A good deal of work has been done by later workers at Dehra Dun on the suitability of other materials for the manufacture of wrapping paper, straw board, heat and sound-insulation fibrous paddings, etc.

Useful work on the deterioration of paper by chemical and biochemical agencies was carried out by Miss Manek Mehta[2], in 1920, in collaboration with Sudborough, Rudolf and Fowler, at the Indian Institute of Science, Bangalore.

The Indian Central Cotton Committee established the Technological Laboratory at Bombay in 1920 and towards the close of the first quarter of the century, valuable information on the mechanical, chemical and technological aspects of cotton fibre was being published. The contributions of Dr. A. J. Turner and his collaborators[3] on the physical and mechanical properties of cotton fibre have become classical.

Research institutions interested in cellulose research and established during the second quarter of the century are : University Department of Chemical Technology, Bombay ; Jute Laboratories, Calcutta ; Shri Ram Institute for Industrial Research, Delhi ; and National Chemical Laboratory, Poona. In Bombay, cellulose research from the textile chemist's point of view has been carried out by Venkataraman and collaborators[4], Desai and collaborators[5] (substantivity of dyes for cotton), Nabar[6], and Mhatre[7] and collaborators (oxidative properties of cellulose with particular reference to bleaching process and physico-chemical properties, like wetting power). The chemical constituents of jute fibre and the molecular structure of jute cellulose have received the sustained interest of workers at Calcutta, notably Sarkar[8], Macmillan[9], Sen Gupta[10], Das[11], and Sen[12].

Indian chemists working in the textile research laboratories at Manchester and Leeds in England, and Princeton in U.S.A. have made valuable contributions. Noteworthy among them are C. K. Patel's work[13], in collaboration with Scholefield, on photochemical oxidation of cellulose in the presence of certain orange and yellow vat dyes ; studies on thermal oxidation by Nabar[6] and D. N. Mehta[14] in collaboration with Turner ; adsorption of dyes on cotton in the presence of electrolytes by A. M. Patel[15], in collaboration with Niels ; hydrolytic study of cellulose by P. C. Mehta[16] with Pacsu ; and on the molecular structure of cellulose with special reference to the role played by adsorbed moisture, by Sen[12], Banerjee[17] and others.

Microbiological research on jute and cellulose at Calcutta[18] and Kanpur, since 1940, is also noteworthy. The Technical Development Establishment Laboratories, Kanpur are engaged on the assessment of rot-proofing and fungicidal treatment of cotton *dosooti* against weathering, mainly with a view to increasing the life of Service tents. At a conference of Commonwealth countries, held in India in 1946, it was pointed out that apart from attack by micro-organisms, there is considerable loss in strength of tentage fabric due to exposure to sun's rays. It was decided to institute studies at Kanpur on the mechanism of changes brought about in the cellulose molecule by exposure to ultra-violet rays and to devise methods by which such deterioration can be minimized. Valuable information on the mechanism of cellulose deterioration has already been gained, and further work is in progress. The mechanism of cellulose destruction by termites and fungi is also under investigation (Subramanian, T. S., personal communication).

Substantial progress in research as applied to paper and rayon industries has been made in recent years. The progress has kept pace with the considerable expansion that has taken place in the paper industry ; more recently, rayon factories have been established in Travancore, Bombay and Hyderabad.

The CSIR Cellulose Research Committee

The Cellulose Research Committee was constituted by the Council of Scientific & Industrial Research (CSIR), in 1940, under the chairmanship of Lala Shri Ram. The subsequent chairmen of the Committee were: Dr. Nazir Ahmed, Dr. S. Krishna, Dr. Lavji Thoria and Dr. B. K. Vaidya; Dr. Vikram A. Sarabhai is the present Chairman. In the early stages, the Committee was primarily interested in initiating researches on raw materials for the rayon industry. The scope of the Committee was later extended to fundamental and applied investigations on all aspects of cellulose and related materials.

At the instance of the Committee, Dr. Thoria made a survey of suitable sites in India for the establishment of rayon factories. He recommended Alwaye in Travancore, Kalyan in Bombay and Navsari in Baroda as suitable places for the industry. Proposals to set up three rayon factories based on the viscose process were made in 1942 and of these, two have matured.

A pilot plant for the production of chemical cotton and for evaluating the suitability of cotton linters and other cellulosic raw materials for paper manufacture, was acquired by the Council and set up in the National Chemical Laboratory at Poona.

The four principal research schemes promoted by the Committee are: (i) Survey of cellulosic raw materials (Indian Central Cotton Committee Technological Laboratory, Bombay) (ii) Study of Indian linters (Indian Central Cotton Committee Technological Laboratory, Bombay) (iii) Preparation of alkali- and water-soluble cellulose ethers (Sayaji Technological Institute, Baroda) and (iv) Anatomical study of cellulosic raw materials (Forest Research Institute, Dehra Dun).

(i) Karnik in collaboration with Ahmed and Sen, carried out investigations on the preparation of pulp from indigenous woods, such as fir, spruce, *salia* and *karai* by sulphite and caustic soda treatments. The yield of pulp varied from 30 to 46 per cent, while the alpha-cellulose content of the three pulps varied from 76 to 86 per cent, and the ash content, from 0.13 to 0.60 per cent. A number of varieties of bamboo (manwel, thorny and kamti), reeds, eetta grass (from Travancore) and two other grasses (from Mysore) gave good pulps containing 93 per cent alpha-cellulose with low ash (0.1–0.3%). A process for preparing high-grade pulp from bagasse, yielding a pulp containing 90 per cent alpha-cellulose and 0.3 per cent ash, has been worked out. Jute and hemp fibres have given excellent pulps and have proved to be the best among the cellulose-bearing materials examined so far; their prices are, however, too high for utilization by the cellulose industry. Among the straws, wheat straw has given results comparable with bagasse. Stalks of castor, cotton and sunn-hemp have also given promising results; the materials can be pulped under high pressure. Kazi grass and aloe leaves give

pulps suitable for paper, but not for rayon. The pulp from bamboo, cetta grass and bagasse compare favourably with imported pulp in respect of alpha-cellulose and ash content; chemical characteristics, such as cuprammonium fluidity, copper number and pentosan, and solubility in alkali are within the permissible limits for commercial pulps. Viscose as well as secondary acetates have been prepared from cellulose, while transparent materials with the desired characteristics have also been made.

(ii) The second scheme of the Committee relates to the study of linters from different varieties of cottons grown in India. Of the eleven species examined (six *hirsutum* and five *desi*), *hirsutum* gives high yield of linters. A suitable process has since been worked out for the utilization of linters, and all the available material finds a ready market in the manufacture of acetate rayon.

(iii) Work on the preparation of alkali and water-soluble cellulose ethers was begun at Baroda, and an economic process for the production of diethyl sulphate, required for the preparation of ethyl cellulose, has been worked out. For the preparation of alkali cellulose, absorbent cotton mercerized with 25 per cent caustic soda for 48 hr. may be employed; after drying in vacuum, the material is suitable for ethylation. Pilot plant work on the preparation of alkali cellulose by this process is to be instituted shortly, probably at the Shri Ram Institute for Industrial Research, Delhi.

(iv) The fourth scheme on anatomical study of cellulosic raw materials was undertaken by Vyas and Sond, in collaboration with Dr. Chowdhury and Dr. Bhat, at the Forest Research Institute, Dehra Dun. The scheme included the examination of bamboo pulp, suitably admixed with parenchyma, for use in paper industry. Two varieties of bamboo (*Dendrocalamus strictus* and *Bambusa nutans*), one hardwood (*Boswellia serrata*) and one softwood (*Picea morinda*) were the materials taken up for study. The fibrous and parenchymatous tissues were separated mechanically and their characteristics were independently examined. The fibres were digested with sodium sulphite and sodium carbonate, and the pulp mixed with parenchymatous tissue in the proportion of 68 : 82 for paper manufacture.

A process has been developed at Dehra Dun for the production of news-print from the mixed pulp of bamboo and bagasse. The suitability of this process for news-print production has been demonstrated by printing a complete edition of the "Statesman" on paper produced at the Forest Research Institute.

Suggestions for further research

Some observations and suggestions, endorsed by the Cellulose Research Committee in 1955 and again in 1956, on the policy of promoting cellulose research may be mentioned.

Research with a bias towards industrial applications should be encouraged, though the ultimate approach in all cases would be basic. A good illustration of this is furnished by the problem of imperfect mercerization of cotton, commonly met with in the textile industry. To study the influence of various cultural and environmental conditions on cotton, one has to go into the fundamental changes brought about in the molecular structure of cellulose; such changes are best investigated by mechanical, optical and X-ray methods.

The research committees are reorganized once in three years, but it has been felt that a minimum term of five years is necessary for the chairman and members of the Committee to acquaint themselves fully with the problems under purview, initiate new problems and progress them to the stage of obtaining commercially useful results. Often it takes a long time to collect basic information on the scientific approach towards a project and its implications in terms of economic possibilities. The recommendation of the Second Reviewing Committee of the Council of Scientific & Industrial Research, namely, that it is desirable for the Council to have a certain amount of guiding hand in individual problems investigated under its auspices, is fully endorsed.

With regard to fresh schemes to be sponsored by the Committee, a welcome change has been brought about by the present Chairman, according to which, the Committee would discuss and evaluate a scheme only after it has been put through a critical examination at a symposium. The Committee would furnish, from time to time, suggestions on specific problems which in their opinion are likely to bear fruitful results. Co-ordination between various centres of research is necessary and proposals of the Reviewing Committee that there should be a representative of each research committee on the Board of the Council merits consideration. Among other proposals made by the Reviewing Committee, the one on liaison also deserves serious notice. It seems that more than one liaison officer would be necessary to visit places and keep in close touch with the development of research schemes in various organizations of the Council.

Cellulose industries

The present position of cellulose industries and their future requirements under the second Five-Year Plan were discussed and approved at a meeting of the Committee in 1956, on the basis of an outline plan drawn up by the Chairman.

The seven principal cellulose industries considered in this plan are: paper, rayon, nitrocellulose, alkyl celluloses, pulp, plastics, and industries dealing with textile fibres other than cotton, such as jute. Suggestions relating to the requirements for the expansion of the first three industries, which are already well established, are based on the quantities of finished products imported on account of the limited capacity of

factories in India, at present. For the new alkyl cellulose and pulp industries, although some experimental data are available from schemes sponsored by CSIR during 1941–50, further investigations appear to be necessary.

The finances required for research and development with respect to these industries may be divided into three parts : (i) laboratory research, (ii) pilot plant investigation, and (iii) full plant trials. From the viewpoint of cost, however, (i) and (ii) together form a negligible part of the expenditure required to establish new plants or modify or expand old ones. The estimates of cost on the three parts may be apportioned on the following basis : (i) Laboratory research—Rs. 10,000 per annum per project for five years. (ii) Pilot plant investigation—Rs. 20,000 per annum per project for six months to one year (exclusive of the cost of equipment, which varies with the nature of the project). (iii) Commercial plant establishment to be based on present capital investment figures.

Cellulose derivatives—For the alkyl celluloses and pulp industries, three schemes of research and three pilot plant trials have been envisaged. The cellulose derivatives considered are : (i) cellulose ethers, (ii) cellulose esters (other than acetate), and (iii) carboxyl methyl cellulose (C.M.C.). These derivatives are used in textile sizing and finishing operations to a limited extent at present. Investigations may be carried through to the pilot plant stage during the current Plan period. Investigations on the preparation of cellulose ethers were financed by the Council during 1943–45 and useful results have been obtained. It is hoped that the work will be taken to the pilot plant stage during the next two or three years at the Indian Central Cotton Committee Technological Laboratory, Bombay and the Shri Ram Institute for Industrial Research, Delhi. The financial requirements for the three schemes (for five years) have been estimated as follows : laboratory research, Rs. 3,00,000 ; pilot plant trials, Rs. 2,00,000.

Mechanical and chemical pulps—At present, mechanical and chemical pulps required for paper and rayon industries are not being produced in India. During 1941–50 a scheme on the examination of indigenous cellulosic materials for their possible use in the pulp industry was in operation at the Indian Central Cotton Committee Technological Laboratory, Bombay. The investigations were not pursued beyond the pilot plant scale. It would appear, however, that there is need for further research and development work in this field, and it is suggested that six research schemes (two for mechanical pulp and four for chemical pulp) involving a total sum of Rs. 3,00,000 may be sanctioned and a further sum of Rs. 2,00,000 may be provided for pilot plant trials. Attempts should be made to secure the help of the private sector for using available equipment for large scale trials.

Paper, rayon and nitrocellulose—These three industries are fairly well established in the country, but further expansion is essential for attaining self-sufficiency in these commodities. An idea of the capital needed for the purpose may be obtained from current investment figures and the rated capacities of the manufacturing units. Thus in the paper industry, the present investment is Rs. 22 crores for an annual production of 1,36,000 tons. For an additional 1,10,000 tons, envisaged under the second Five-Year Plan, *c.* Rs. 20 crores extra capital would be necessary. Similarly, for the rayon industry, for an extra 1,785 tons production, the capital needed is of the order of Rs. 13 crores.

Data for the manufacture of nitrocellulose are not obtainable as this material is, at present, produced solely for the manufacture of explosives in government factories ; explosives valued at Rs. 2 crores are annually imported. Nitrocellulose with low degree of nitration is not produced in any large scale as lacquer and plastic industries which use these products have not been established in this country. The requirements with respect to lacquers, etc. are met by imports.

Research and pilot plant work in respect of these three major cellulose industries should be supported by both public and private sectors. The need for establishing lacquer and plastic industries based on nitrocellulose is undoubted.

Bast and other cellulose-bearing fibres—Except for the jute industry, no other organized industry based on bast fibres exists at present. Attempts have been made to examine the possibilities of utilizing linseed, bagasse, straw and other bast as well as leaf fibres. There is considerable scope for developing fibre industries on a cottage scale in villages.

The present position of cellulose industries and suggestions for their development during the current Plan period are given in Table 1.

Cellulose Research Abroad

Early work, notably by Irvine and Hirst[19] and Haworth[20] in England, Staudinger[21] and Freudenberg[22] in Germany, and Kuhn[23] in Switzerland, supplemented by the classical X-ray studies of Mark and Meyer[24] in Germany and Hermans[25] in Holland, has produced the basic concept of the miceller structure of the cellulose molecule. Micelles are considered as statistically distributed regions of a latticed order in a mass of approximately paralled chain molecules. In such an arrangement, 'crystalline' regions alternate with 'amorphous' regions which are not too orderly. The crystalline regions have a preferred orientation with respect to the axis of the cellulose fibre. The questions which are yet to be answered are : how do the crystalline and amorphous parts of cellulose respond to mechanical and chemical treatment ? What is the relation between the strength, degree of orientation and amount of

TABLE 1—CELLULOSE INDUSTRIES : PRESENT POSITION AND SUGGESTIONS FOR DEVELOPMENT DURING THE CURRENT PLAN PERIOD

	Present position			Development		
	Annual production *tons*	Annual import		Research *lakh Rs.*	Pilot plan trials *lakh Rs.*	Plant installation *lakh Rs.*
		Qty. *tons*	Val. *lakh Rs.*			
PAPER						
Newsprint Packing and wrapping papers Writing paper Straw board	1,56,000	1,10,400	1,300	←	20 →	2,000
RAYON						
Viscose (cont. filament, cut staple, high tenacity)	8,000	18,000	1,500	..	..	..
Acetate Cuprammonium	..	n.a.	n.a.	←	13 →	1,300
NITROCELLULOSE						
Explosives	n.a.	n.a.	200	←	5 →	200
Lacquers	..	n.a.	..	..	..	100-200
PLASTICS						
Viscose, acetate and cellulose	n.a.	n.a.	n.a.	←	5 →	200
CHEMICAL DERIVATIVES	..	n.a.	n.a.	3	2	
PULP						
Mechanical and chemical	..	6,000-8,000	n.a.	3	2	600-800
BAST, LEAF AND OTHER FIBRES						
Jute	10,50,000	..	..	←	800–1,000	→
Coconut	n.a.	..	..			

crystallinity in a cellulose fibre? What do the large spacings, indicated by X-ray diffraction studies signify? What determines the substantivity of materials strongly adsorbed by cellulose?

The mechanical properties of cellulose in the form of ramie, flax, cotton and viscose, as well as other derivatives, have been extensively studied both in Europe and in U.S.A., and although useful information on the practical uses of the fibres has become available, their complex behaviour under load is not predictable in terms of the corresponding visco-elastic models.

A good deal of work has been reported on the molecular weight, average degree of polymerization, and statistical distribution of chain length of cellulose in the dispersed state. Such studies provide an insight into the physical properties of materials made from cellulose dispersions, such as paper and regenerated cellulose fibres.

On the chemical side, the work on the modification of cellulose, carried out in the Southern Regional Laboratories, New Orleans, U.S.A., is noteworthy. Partial replacement of OH groups in the cellulose molecule by phosphoryl and amino groups yields yarns and fabrics with unusual properties; treated cellulose containing amino groups takes up the acid dyes used for wool dyeing. Other cellulose derivatives which have been developed commercially are: water-soluble carboxyl methyl cellulose, extensively used in the textile industry, and alkyl celluloses largely used in lacquers.

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Discussion

Shri K. S. Varadachar: The Defence Department is keenly interested in finding sources of cellulose, other than cotton waste for the production of nitrocellulose. The TDE, Nilgiris would offer full assistance in evaluating materials and in development work. The important requirements are: alpha-cellulose content, not less than 90 per cent: lignin content, low; and ash content, not more than 0.25 per cent.

Dr. Lavji Thoria: I do not think that work on linters is necessary any longer, as delinting plants have already been put up in India and practically the entire production of linters is used up by *Sirsilk Ltd.*, Hyderabad; in fact, they are short of linters. This is a natural limitation imposed by the fact that the seed of *desi* varieties of cotton is almost linterless. We can recover linters only from the seeds of hybrid varieties.

As regards nitrocellulose, it is advisable to use some cheaper cellulose raw material instead of cotton waste which fetches a good price. Wood pulp which is equally good and perhaps more stable, is used in Germany for making nitrocellulose.

Shri O. P. Gupta: In considering alternative sources of cellulose for the production of nitrocellulose, one must not overlook the fact that the present plant and machinery are designed to use only cotton waste. Any change in raw material may involve costly changes of plant.

Structure and Mechanical Properties of Cellulosic Fibres : Some Problems

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The following problems, relevant to the understanding of the performance of cellulosic fibres, have been reviewed : (i) fibre-to-fibre interactions in such assemblies as slivers and yarns ; (ii) improved methods for determining mass-order distributions in relation to mechanical behaviour ; and (iii) structural imperfections and fracture occurring when fibres are broken in flexure or tension.

Recent research on the structure and mechanical properties of cellulosic fibres has focussed attention on three major fields. The first relates to the interaction between fibres in processing and in fibre assemblies, such as yarns and fabrics. The second concerns the internal structural order in fibres and the relation of this to stress relaxation phenomena which control, to a large extent, the time dependency of mechanical behaviour. The third relates to the influence of structural imperfections on the instrinsic strength of cellulosic fibres.

These three fields are briefly discussed here and specific issues in which progress should lead to a better understanding of fibre performance have been indicated.

Fibre-to-fibre Interactions

Generally speaking, in fibre-to-fibre interactions, two properties are important. One is the inter-fibre friction which is believed to be influenced by surface properties. It is known, for example, that modification of cotton fibre surface by removal of waxes, application of colloidal silica or addition of 'lubricants' generally influences processing behaviour in operations in which the fibres 'drag' on each other.

In this field, a number of questions remain to be answered. Basically, there is the problem of measuring fibre-to-fibre friction and the forces required to produce relative movement between fibres under various circumstances[1]. What is involved, for example, in the mechanism of improving processing behaviour by the removal of waxes or the addition of colloidal silica ? Do 'lubricants' actually lubricate or do they have the effect of increasing the adhesion between fibres ?

In recent years, the geometrical configuration of fibres as indicated by fibre crimp (or kinkiness) has received extensive attention. This has been made possible by the development of methods for the measurement of crimp. Evans and Montgomery[2] have evaluated the force and the extension needed to remove crimp from fibre. Alexander *et al.*[3] have devised a method of evaluating 'effective crimp amplitude and wave length' by an ingenious optical method. These advances show promise of permitting certain fundamental questions regarding crimp to be answered. How do various fibres resist loss of crimp during processing into yarns or fabric? How much crimp should a fibre have for optimum processing performance? It is known, for example, that synthetic staple fibres need to be crimped before they can be satisfactorily processed on either the cotton or the woollen systems. On the other hand, wool fibres, in many instances, possess so much crimp that the crimp needs to be suppressed by 'resting' the wool in roving or yarn stages. Apparently, there is an optimum level of crimp which is most advantageous for processing.

Mass-order distribution and stress relaxation

Howsmon and Sisson[4] have described the internal structure of cellulosic fibres in terms of mass-order and order-orientation distribution diagrams. These diagrams generally indicate what portions of the fibres are ordered to different extents and how these portions are oriented with respect to the long axis of the fibre. By means of these diagrams, they have been able to explain moisture absorption behaviour, chemical reactivity, X-ray crystallinity data and, to a limited extent, mechanical properties.

The mass-order distributions which Howsmon described are generally based on solubility and accessibility data with various chemical media. However, improved methods are needed for determining more precisely the mass-order distributions and relating them to mechanical behaviour. Some progress has been made in this direction by Whitwell and Lemicska[5] who have attempted to predict accessibility or mass-order distributions from stress relaxation data. This prediction is based on the assumption that the less-ordered portions of the fibre contain the elements of low relaxation time and that stress relaxation for a given fibre is related to the relaxation time of various structural elements in the polymer. Further investigation in this direction seems to promise more useful information on the relationship between fibre structure and mechanical behaviour.

Structure Imperfections and Strength

It is well known that the theoretical strength of cellulosic fibres based on the average cross-section of the fibre is much greater than that observed when strength tests are made. It is generally believed that this deficiency of the fibre is due to various structural imperfections which exist along

the fibre. In the case of cotton, these have been shown to be related to fibre reversal—a structural characteristic of all cotton fibres[6]. Recently, attention has been given to a more generalized treatment for all polymeric substances by George[7]. These investigators have studied the fracture processes occurring when fibres are broken in flexure or tension. This subject should receive considerably more attention, since fibre strength is an important property for many practical applications.

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Discussion

Shri K. S. Bhujang: How was the mass-order distribution obtained?

Dr. H. Wakeham: This has been obtained from various existing data. In the extreme right of the distribution, for values of high crystallinity, data on X-ray diffraction have been used. On the left of the distribution for regions of low crystallinity, available data on accessibility have been used.

Shri K. S. Bhujang: Using the iodine absorption method, we found that mature and immature fibres both give the same ratio of amorphous to crystalline regions. However, immature fibres absorb more acid dye than mature fibres.

Dr. H. Wakeham: The only difference between immature and mature fibres is in their wall thickness. However, even immature fibres contain enough cellulose in their secondary walls to absorb iodine and there is no reason why a different proportion of amorphous to crystalline regions should be expected with immature fibres. The larger absorption of acid dye is due to entirely different reasons.

Dr. P. K. Choudhury: How do stress-strain hysteresis curves for cotton and viscose differ?

Dr. H. Wakeham: The shapes of the curves are very similar. However, energy absorption is higher for viscose.

Dr. V. B. Chipalkatti: How is accessibility determined?

Dr. H. Wakeham: There are many methods for measuring accessibility and the value of accessibility obtained varies according to the reagent used for measuring it.

Dr. K. R. Ramanathan: What do you mean by crimp?

Dr. H. Wakeham: Crimp is the wavy shape or kinkiness observed along the length of fibres. The dimensions of the kinks are of the order of 1 mm. or more. Crimp is distinct from surface irregularity, as seen by microscopic examination of the fibre cross-section.

Dr. V. B. Chipalkatti: What was your idea in studying crimp? To improve cotton or study its structure?

Dr. H. Wakeham: We are trying to improve cotton mechanical processing.

Relation Between Molecular Orientation and Mechanical Behaviour of Mercerized Cotton Fibres

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Investigations on crystallite orientation in mercerized cotton and the relation which orientation bears to the load-extension behaviour of the fibre, are in progress in the laboratory. It has been observed that as the crystallite orientation factor increases, the fibres become stiffer, stronger and less extensible.

It is well known that the degree of molecular orientation in textile fibres is intimately related to the mechanical properties of the fibres. In the case of raw cotton, the relation between tensile strength and orientation has been studied by several workers[1, 2] and the measurement of orientation by means of X-rays has been become a trade test in one country[3]. Unfortunately, this type of study is mostly based on the use of a parameter for orientation (40% X-ray angle of 002 interference) which does not possess a clear physical meaning. However, it is possible to measure crystallite orientation in cotton in terms of more clear and well-defined physical concepts[3, 4]. Investigations on crystallite orientation and the relation which orientation bears to the load-extension behaviour of fibre are in progress in the ATIRA laboratories. Mercerized cotton is being used in preference to raw cotton because stretching of alkali-swollen fibres to various extents, prior to washing, enables the preparation of fibres with widely differing orientation values[4]. Studies are also proposed on raw cotton, with emphasis on load-extension behaviour, rather than on tensile strength[3].

Preparation of Samples

Samples are prepared by swelling cotton fibre for 5 min. in 25 per cent caustic soda in a totally slack condition, then stretching to the desired level, and washing and drying under stretch. By means of this technique, almost complete conversion is secured from the lattice of cellulose I to that of cellulose II. This simplifies the evaluation of crystallite orientation. The stretch level is reckoned as percentage of original dry length of sample.

The mercerizing process is carried out on small groups as well as larger bundles of parallel fibres and on small skeins of plied yarn. More importance has been given to fibre studies for obvious reasons. Special devices have been made whereby bundles of strictly parallel fibres can be swollen (in a slack condition) in alkali and stretched and washed on the Instron tensile tester. This machine permits the accurate control of stretch and also measures the force needed to cause this stretch. A device has also been made for manually stretching a small number of alkali-swollen fibres with great precision. Plied yarn skeins can be impregnated with caustic soda and stretched to the desired level by means of a third device which is also used in conjunction with the Instron tensile tester.

Measurement of Crystalline Orientation

The theory behind the determination of crystallite orientation has been described elsewhere[4]; only the results are given here. If α is the angle made by the b-axis of the crystallites with the fibre axis, then the X-ray diffraction study cannot unambiguously determine the distribution function of α; but it can determine a weighted mean angle $\overline{\alpha}$ in terms of the intensity distribution I (β) and I (γ) of the 101 and 101 interferences, where β and γ are azimuth angles, i.e., angles reckoned from the equator of a flat film pattern. The relation between $\overline{\alpha}$ and the intensity distribution is:

$$\overline{\sin^2 \alpha} = \frac{\int_0^{\pi/2} I(\beta) \cos \beta \sin^2 \beta \, d\beta}{\int_0^{\pi/2} I(\beta) \cos \beta \, d\beta} + \frac{\int_0^{\pi/2} I(\gamma) \cos \gamma \sin^2 \gamma \, d\gamma}{\int_0^{\pi/2} I(\gamma) \cos \gamma \, d\gamma} \quad (1)$$

The orientation factor of the crystallites can be conveniently defined as:

$$f_x = 1 - \tfrac{3}{2} \overline{\sin^2 \alpha} \quad (2)$$

The intensity distributions I (β) and I (γ) are measured by means of a specially constructed Geiger Counter diffractometer in which the specimen can be rotated in a direction perpendicular to the beam axis so that various portions of the diffraction arc under investigation sweep past the window of the counter which is aligned at the proper angle. This instrument was made in the laboratory, but it is basically similar to a published design[5]. Measurements are also being made of intensity distributions around the 002 interference, since this can be used for a simple, though approximate, computation of orientation.

Mechanical Behaviour

The mechanical behaviour of single fibres (chosen at random from the same bundle used for X-ray measurements) is under test using the Instron tensile tester. This instrument can be used to plot the load-

extension curve of the specimen at a constant rate of extension until rupture takes place. Special devices have been made in order to ensure a constant test length from fibre to fibre. The loan-extension diagram of an average fibre, i.e., a fibre which possesses the average tensile strength and extensibility, is taken as representative of the group of fibres tested. From this curve, the fibre stiffness and creep properties can be evaluated.

Since the study is still in progress, no quantitative results are available at present. However, it has been observed that as the crystallite orientation factor increases, the fibres become stiffer, stronger and less extensible.

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Discussion

Shri T. S. A. Padmanabhan: We are trying to put 0.5 to 0.6 per cent of manganese on cotton by first steeping it in manganese sulphate and then treating with sodium hydroxide. Can X-ray diffraction be used to know the mode of combination of the metal with the fibre?

Dr. T. Radhakrishnan: For getting X-ray diffraction of sufficient intensity, our experience so far indicates that the metal should have an atomic number of 50 or above to give high scattering. The material should also be present in the fibre to the extent of more than 1 per cent by weight. The best thing to do is to try out your sample.

Shri R. G. Manudhane: Cotton dyed with mineral khaki does give X-ray diffraction patterns.

Shri K. Manivannan: Has bending or flexing any effect on orientation?

Dr. T. Radhakrishnan: The process is complicated and still remains to be investigated.

Light Scattering Studies of Cellulose Solutions in Concentrated Acids: Part I—Wood Pulp & Cotton Cellulose in Phosphoric & Sulphuric Acids. PIJUSH KANTI CHOUDHURY (Calcutta).

J. sci. industr. Res., **16B** (1957), 289.—Light scattering studies on cellulose solutions in concentrated sulphuric and phosphoric acids have indicated the formation and growth of a large-sized and extensively branched polymer of 5-hydroxy methyl furfural. The formation of the polymer has been confirmed by the absorption spectrum of the solution and optical density measurements. *(Abstract)*

Studies in Cellulose Chemistry : Part I—Certain Observations on the Formation of Cellulose Nitrate from Cellulose. T. S. A. PADMANABHAN, S. K. RANGANATHAN, T. N. RAWAL & L. R. SUD (Kanpur).

J. sci. industr. Res., **16B** (1957), 414.—Adopting Davidson's method of nitrating cellulose, nitrates containing not more than 12 per cent nitrogen have been obtained. Reduction of the water content of the nitrating solution, by increasing the strength of phosphoric acid present in it, favours the formation of cellulose nitrate with a higher nitrogen content. The nitrating content should contain a minimum of 5 per cent phosphoric acid for obtaining soluble cellulose nitrates. Experiments undertaken to determine the extent of degradation of cellulose during nitration have not yielded conclusive results. A mathematical relationship connecting viscosity, nitrogen content and molecular weight of cellulose nitrate seems to be a prerequisite for obtaining evidence on cellulose degradation. *(Abstract)*

Studies in Cellulose Chemistry : Part II—Alkali-sensitive Linkages in Irradiated Cellulose

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Cellulose undergoes two types of changes on exposure to ultra-violet light from a mercury arc lamp. Some glucosidic linkages in the cellulose molecule are ruptured and some are weakened. The latter are of two types in regard to their behaviour during storage in air or oxygen : those that suffer cleavage, and those that are stable. Both these types, however, are sensitive to alkali and are removed by boiling with alkali.

In the course of investigations undertaken in these laboratories on the mechanism of actinic degradation of cellulose, and on the methods of controlling such degradation, it was found necessary to select a suitable method for measuring the chain length of cellulose. A critical review of the literature, particularly contributions from the Shirley Institute, revealed that the most satisfactory method is the one based on the measurement of viscosity of cellulose nitrate dissolved in acetone. The results obtained by using this method, the factors contributing to a high degree of nitration, and the solubility of the nitrated product in acetone, are described in an earlier communication from these laboratories[1]. The present paper deals with the study of changes in chain length brought about in cellulose when irradiated by a mercury vapour lamp.

Stillings and Van Nostrand[2] showed that irradiation not only caused cleavage of some of the glucosidic linkages of the cellulose molecule, leading to a fall in the degree of polymerization (D.P.), but also weakened a few others. These weakened linkages broke down during the post-irradiation period, leading to a further fall in D.P. Davidson[3] studied the changes suffered by cellulose when reacted with oxidizing agents, such as potassium dichromate and sodium hypochlorite, and came to the conclusion that some glucosidic linkages are ruptured and simultaneously, some others are weakened : the weakened linkages were sensitive to alkali and could be removed by boiling with 1 per cent aqueous sodium hydroxide.

On the basis of the parallelism in the transformations caused by ultra-violet light and oxidizing agents, it was of interest to investigate whether

the weakened linkages arising from irradiation were also sensitive to alkali. In a preliminary note[4] on the subject, attention was drawn to the alkali-sensitivity of linkages and to the results that seemed to show that the fall in the D.P. of cellulose during storage after irradiation approximated to the fall in D.P. caused by boiling cellulose in alkali immediately after irradiation. Investigations have since shown that while all the weakened linkages are 'removed' by alkali, a certain proportion of them do not take part in the Stillings and Van Nostrand's post-irradiation effect[2].

Materials and Methods

Source of cellulose—The samples used in the investigation were derived from highly scoured, undyed cotton fabrics, *dosooti* and satin drill, both weighing *c.* 7 oz. per sq. yard. These were boiled with 1 per cent sodium hydroxide solution to free them from weakened alkali-sensitive linkages which may be present as a result of chemical processing or finishing during manufacture. The process of boiling was repeated until no further fall in D.P. took place as indicated by the intrinsic viscosity of the corresponding cellulose nitrate[1].

Source of ultra-violet radiation—Hanovia High Alpine Sun mercury vapour lamp, manufactured by Messrs *Hanovia Ltd.*, Slough, U.K., was used as the source of ultra-violet light. A powerful spectrum in the region of 2,200 A. in the ultra-violet to 20,000 A. in the infra-red, with bright spectral lines at 2,536 A. and 4,358 A., is obtained from the lamp. The intensity of the lamp at a distance of 30 cm. (at which the fabrics were irradiated) was measured by the method of Wagner *et al.*[5] In the absence of data on the intensity of sunlight at Kanpur (26°26′ : 80°22′) comparison was made with the data for Shahjahanpur (26° : 80°). It will be noted (Table 1) that total radiation from the lamp at a distance of 30 cm. is about 5 times as great as that from the sun. In the ultra-violet region, the intensity is about 58 times as much as that from the sun.

Irradiation of fabric—The fabric was placed at a distance of 30 cm. vertically below the lamp, the surface area of the fabric exposed at this distance being *c.* 1,000 sq. cm. The temperature at the surface of the fabric was maintained at *c.* 30°C. with the help of a fan and the influence of thermal factors[6] was thus eliminated.

Post-irradiation storage—Immediately after irradiation, the fabric was dethreaded and shredded to bits. After thorough mixing, 2–3 g. were taken and converted into cellulose nitrate. The rest of the sample was spread uniformly in a flat dish and stored in a closed space at laboratory temperature (25–30°C.) for observing the post-irradiation (P.I.) effect.

Estimation of fall in D.P.—The samples of cellulose were nitrated according to the procedure described in an earlier paper[1]. The following samples were examined : (i) original sample before irradiation ; (ii) sample taken

TABLE 1—COMPARATIVE INTENSITY OF RADIATIONS FROM HANOVIA LAMP AND THE SUN AT SHAHJAHANPUR

Spectral region	Intensity, *m.w./sq. cm.*	
	Hanovia lamp at 30 cm.	Solar radiation at Shahjahanpur*
Visible radiation	198.9	92.7
Ultra-violet radiation beyond 2900 A.	192.2	..
Ultra-violet radiation below 2900 A.	87.8	..
Total ultra-violet radiation	280.0	4.88
Total visible and ultra-violet radiation	478.9	97.6

* Data supplied by the *India Meteorological Department*

TABLE 2—FORMATION OF ALKALI-SENSITIVE LINKAGES DURING IRRADIATION

Irradiation period *hr.*	Intrinsic viscosity of cellulose nitrates, *dl./g.*		
	Immediately after irradiation	After irradiation and alkali-boiling	Fall due to alkali boiling
0	8.13	8.32	..
4	7.94	7.24	0.70
7	7.83	6.92	0.91
24	6.76	5.89	0.87
31	6.76	6.00	0.76
48	6.38	4.90	1.48
55	6.28	5.43	0.85
72	6.14	4.49	1.65
96	5.62	4.89	0.73
120	5.35	4.07	1.28

immediately after irradiation ; (iii) sample treated with 1 per cent sodium hydroxide immediately after irradiation. This gives an estimate of alkali-sensitive linkages formed during irradiation ; and (iv) samples taken out from storage at definite intervals. Normally 4–5 weeks were required for the intrinsic viscosity to reach constancy. As a matter of caution, the storage was continued for longer periods ; the sample was then boiled with alkali.

Results and Discussion

Alkali-sensitive linkages—Satin drill was used as the source of cellulose in this investigation. During the irradiation, which lasted for 120 hr., samples were drawn at varying intervals, converted into cellulose nitrates before and after boiling with 1 per cent alkali, and the intrinsic viscosities

TABLE 3—ALKALI-SENSITIVE LINKAGES AND POST-IRRADIATION (P.I.) EFFECT

(*material used*, dosooti)

No.	Irradiation period *hr.*	Storage period after irradiation *weeks*	Viscosity of cellulose nitrate, *dl./g.*					
			Before irradiation	Immediately after irradiation	After irradiation & alkali-boiling	After irradiation & storage	After irradiation, storage & alkali-boiling	After irradiation, alkali-boiling, & storage
1	8	9	12.42	11.22	9.42	10.53	..	9.53
2	24	9	12.42	9.30	7.72	8.26	..	7.69
3	24	8	10.09	8.91	6.76	8.04	6.83	..
4	24	10	8.83	7.50	6.67	7.24	..	..
5	24	8	9.02	7.85	6.17	7.28	6.13	6.01
6	31	9	12.42	8.57	7.37	7.16	..	7.26
7	48	9	12.42	7.66	6.53	6.49	..	6.46
8†	48	19	..	8.37	6.61	7.62	6.64	..
9	48	6	9.91	7.76	6.04	6.92	5.94	..

† Material used—satin

determined. In order to reduce to a minimum the effect due to heterogeneity, the fabric was divided into 4 quadrants, each containing 10 sectors of equal area. At each sampling, one sector from each quadrant was cut out and after shredding to bits was mixed thoroughly. The results are given in Table 2.

The difference in viscosity values at zero hour irradiation is due to the heterogeneity of the material. As irradiation proceeds, there is a general fall in D.P. At any interval, treatment of irradiated cellulose with alkali produces a further fall in intrinsic viscosity value, thereby showing that weakened linkages are alkali-sensitive.

Stillings and Van Nostrand's effect—In order to understand the role of alkali-sensitive linkages in the Stillings and Van Nostrand's (P.I.) effect[2], several irradiations of cellulosic fabrics were carried out for periods varying from 8–48 hr. and the intrinsic viscosities of corresponding cellulose nitrates were determined after different periods of exposure. In some cases, the irradiated fabric, after boiling with alkali, was stored for some time and the intrinsic viscosity of the corresponding cellulose nitrate was determined thereafter. The results are given in Table 3.

It will be observed that the intrinsic viscosity suffers a further fall as a result of storage due to cleavage at the weakened glucosidic linkages (Stillings and Van Nostrand's effect[2]). There is also a fall in intrinsic viscosity when the irradiated material is boiled with alkali immediately after irradiation. There is agreement in the values for intrinsic viscosity of materials irradiated and boiled immediately thereafter with alkali, and those irradiated, kept in storage and then boiled with alkali. Where

TABLE 4—STABLE ALKALI-SENSITIVE LINKAGES IN IRRADIATED CELLULOSE

(Irradiation period, 40 hr.; Storage period after irradiation, 7 weeks)

No.	Viscosity of cellulose nitrate, *dl./g.*			
	Before irradiation	Immediately after irradiation	After irradiation & alkali-boiling	After irradiation & storage
1	12.82	9.43	7.48	8.22
2	12.76	9.04	7.54	8.22
3	11.46	8.20	7.08	8.13
4	11.38	8.17	7.03	8.22
5	10.89	7.00	5.93	6.62
6	10.96	6.61	5.93	6.49
7	10.94	6.92	5.53	6.42

the irradiated material was not boiled with alkali before storage, the value obtained for stored material was intermediate between that for the irradiated materials and that of the material irradiated and treated with alkali immediately after. In one case (No. 7, Table 3), the intrinsic viscosity of irradiated material boiled with alkali before storage, was the same as that of irradiated material stored for 9 weeks. It will also be seen that no fall in intrinsic viscosity takes place during the storage of material irradiated and boiled with alkali. These results show that while all weakened linkages arising from irradiation are removed by alkali, a proportion of them does not always take part in the post-irradiation effect. The results, however, do not throw any light on the factors responsible for the formation of weakened linkages which are stable during the post-irradiation storage.

In another experiment, 7 samples of *dosooti* were exposed to 40 hr. irradiation under identical conditions and irradiated samples were stored for 7 weeks. The results of intrinsic viscosity determinations are given in Table 4. It will be observed that in all cases alkali-sensitive linkages, stable during post-irradiation period, have been formed. In two cases (No. 3 and 4), the linkages are exclusively of the stable category. The results do not throw any light on the factors responsible for the post-irradiation effect.

The results summarized in Tables 2–4 confirm the findings of Stillings and Van Nostrand[2] that the effect of ultra-violet radiation on cellulose is twofold : (i) rupture of some glucosidic linkages, and (ii) weakening of some others leading to their cleavage during post-irradiation. Earlier work (unpublished) from these laboratories has shown that the post-irradiation effect does not lead to an increase in the copper number of irradiated cellulose. It appears, therefore, that there is an essential difference between the overall changes taking place in the cellulose molecules during irradiation and subsequent storage.

The results summarized in Tables 3 and 4 show that while all the weakened linkages are removed by 1 per cent aqueous alkali, a proportion of them does not take part in the post-irradiation effect. These may be regarded as being stable during post-irradiation storage and resemble alkali-sensitive linkages present in chemically modified celluloses. In an earlier communication[4], the changes taking place during the storage of irradiated cellulose had been equated with those occurring in material boiled with alkali immediately after irradiation. In the light of the overall evidence reported in this paper, the above conclusion needs to be revised.

While the formation of stable alkali-sensitive linkages has been established, it has not been possible to trace the factors responsible for their formation. Even under identical conditions of irradiation, the proportion of stable weakened linkages varies (Table 4). This may be due to the inherent

heterogeneity in the cellulose fabric or to the topochemical nature of changes which generally take place in cellulose. Although every effort was made to counter the heterogeneity factor by random sampling and averaging of samples prior to nitration, greater refinement in technique and choice of a suitable cellulose source are necessary to throw further light on post-irradiation phenomenon.

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Studies in Cellulose Chemistry : Part III—Hydrated Oxides as Barriers Against Actinic Degradation of Cellulose*

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Hydrated oxides of iron, chromium, copper, manganese, aluminium, tin and titanium were incorporated *in situ* on *dosooti* fabric used in tentage and exposed to sunlight at Kanpur for 2,400 hr. The comparative protective effect of the treatment was assessed by measuring the loss in bursting strength of fabrics. Manganese (hydrated oxide), provided a high degree of protection, while copper, even in small quantities, accelerated actinic degradation of cellulose.

In an earlier paper[1], the changes taking place in the cellulose molecule during and after ultra-violet irradiation were described. The present paper deals with investigations undertaken to prevent the degradative effects of sunlight on cellulose.

Although attempts have been reported[2-7] to prevent actinic degradation of cellulose by various types of barrier treatment, no effort appears to have been made to assess their efficiency in a quantitative manner and to elucidate the pattern of degradation and the mechanism of protective action. A systematic examination of hydrated metal oxides in relation to their barrier properties has been undertaken in the laboratories. Metals showing variable valencies, e.g., iron and chromium, were selected for this study and treated fabrics were exposed to sunlight at Kanpur[8, 9]. Samples were drawn at varying intervals of exposure and examined for their physical and chemical properties.

Experimental Procedure

Cellulose fabric—The fabric used for the construction of Service tents was selected for the study. It is a double warp, double weft, highly scoured cotton fabric, known as *dosooti* (36 in. wide; wt., 7 oz./sq. yd.). It was woven on one beam and was uniform.

* A short note on this subject appeared in *Nature*, 163 (1949), 877.

Method of treatment—Preliminary experiments were carried out to determine the concentration of salt solutions to be employed for depositing the requisite amount of metal on the fabric.

A 5-yd. length of the fabric was immersed in a solution of the metal chloride or sulphate, contained in a 2-bowl padding mangle with nip adjusted to 100 per cent take-up. The treated fabric was air-dried in a horizontal position to prevent any flow of absorbed solution. The dried fabric was then immersed for 10 min. in an alkali solution to convert the metal into insoluble hydroxide. For treatment with chromium, copper, iron and manganese, a 2 per cent aqueous solution of sodium hydroxide was used, while for aluminium, tin and titanium, a 5 per cent ammonium hydroxide solution was employed. The fabric was then given three ends in the padding mangle. It was washed with water till free of alkali and dried at 100–105°C.

Exposure—The outdoor exposure trials were carried out at Kanpur (26°28′ : 80°21′ ; altitude 416 ft. above mean sea level). Treated fabrics and untreated controls were mounted on wooden frames, 1 yard square, and exposed on iron stands 4 ft. above the ground level facing south at an angle of 45°. There were three frames for each treated fabric and the control. The exposure was confined to bright sunshine only, the frames being removed from light during the remaining period. The exposure lasted for 2,400 hr.

Sampling—An area of 30 sq. in. was marked in the centre of each frame and divided into nine equal sections. Three sections from each fabric were cut out in a randomized order, initially at the start of exposure, and later, after every subsequent 400 hr. of cumulative exposure.

Assessment of degradation—The degradation suffered by exposed fabrics was assessed by the estimation of the following :

Bursting strength—After conditioning the samples for 48 hr. at 65–70 per cent relative humidity (RH) and 20°C., the bursting strength of 6 replicates was determined on Mullen's bursting tester (capacity, 800 lb.). The percentage loss in bursting strength suffered by exposed fabrics was calculated.

Cuprammonium fluidity and copper number of exposed fabrics and controls were measured according to the methods of Clibbens and Geake[10, 11].

Tables 1, 2 and 3 give the percentage loss in bursting strength, cuprammonium fluidity, and copper number of exposed fabrics.

Results and Discussion

The treatment of the fabrics with salts does not by itself produce any loss of bursting strength or change in cuprammonium fluidity.

TABLE 1—EFFECT OF TREATMENT ON BURSTING STRENGTH OF FABRIC*

Treatment	Metal content %	Bursting strength (% loss) after exposure for					
		400 hr.	800 hr.	1,200 hr.	1,600 hr.	2,000 hr.	2,400 hr.
Control	..	16	43	60	51	67	65
Manganese	0.04	16	38	50	49	62	59
	0.56	6	16	18	10	18	19
	1.3	11	22	22	23	30	29
Chromium	0.80	35	47	65	55	67	68
Copper	0.82	29	47	91	98	..	..
Tin	0.97	26	53	80	81	..	..
Titanium	0.97	36	51	86	93	..	..
Iron	0.84	0	12	43	50	61	61
Aluminium	0.45	14	24	46	44	57	59

* In all cases, three concentrations of metallic salts were used. Except in the case of manganese, only the values for the highest concentrations tried are given in the table.

TABLE 2—EFFECT OF TREATMENT ON CUPRAMMONIUM FLUIDITY*

Treatment	Metal content %	Cuprammonium fluidity after exposure for						
		0 hr.	400 hr.	800 hr.	1,200 hr.	1,600 hr.	2,000 hr.	2,400 hr.
Control (Untreated)	..	3	13	19	28	29	33	35
Manganese	0.04	8	17	23	27	30	36	36
	0.56	6	11	13	15	17	18	18
	1.30	7	12	13	14	18	16	17
Chromium	0.80	9	26	32	32	34	39	38
Copper	0.82	11	31	35	44	44	..	..
Tin	0.97	10	26	35	39	40	..	..
Titanium	0.85	7	24	30	36	34	..	..
Iron	0.84	7	13	16	20	21	25	25
Aluminium	0.45	6	13	17	28	24	33	35

* In all cases, three concentrations of metallic salts were used. Except in the case of manganese, only the values for the highest concentrations tried are given in the table.

TABLE 3—EFFECT OF TREATMENT ON COPPER NUMBER*

Treatment	Metal content %	Copper number after exposure for						
		0 hr.	400 hr.	800 hr.	1,200 hr.	1,600 hr.	2,000 hr.	2,400 hr.
Control	..	0.06	0.80	1.14	2.34	2.79	3.64	3.63
Manganese	0.04	0.12	0.79	1.24	2.10	2.19	2.59	3.25
	0.56	0.02	0.04	0.04	0.03	0.02	0.06	0.18
	1.3	0.02	0.04	0.03	0.03	0.02	0.02	0.00
Chromium	0.80	0.02	1.39	2.20	2.58	2.97	3.34	4.29
Copper	0.82	0.26	1.90	3.42	7.49	9.68	..	..
Tin	0.97	0.31	1.16	2.42	4.05	3.34	..	..
Titanium	0.85	0.14	1.81	2.01	3.16	3.66	..	..
Iron	0.84	0.11	0.62	0.96	1.53	2.08	2.60	2.89
Aluminium	0.45	0.11	0.58	0.87	1.92	2.30	2.93	3.19

* In all cases, three concentrations of metallic salts were used. Except in the case of manganese, only the values for the highest concentrations tried are given in the table.

As a result of exposure to sunlight for 2,400 hr., the untreated control fabrics suffered a loss of 65 per cent in bursting strength (Table 1). Among the treated fabrics, those containing hydrated oxide of manganese suffered the least loss. The most effective concentration of the hydrated oxide was 0.56 per cent. Even with a lower concentration (0.04%), the loss suffered was much less than that of the control or of fabrics treated with other metallic hydrated oxides.

Fabrics treated with hydrated oxides of chromium, copper, tin, titanium, iron and aluminium did not offer any protection. Copper, tin and titanium, accelerate actinic degradation at certain concentrations.

From a study of the results obtained, it appears that the exposure to sunlight leads to a slow oxidation of the functional hydroxyl groups of glucose units of the cellulose chain into carboxyl groups through the intermediate stage of aldehydes/ketones. The gradual increase in copper number with increasing exposure to sunlight, noticed in all cases (except in fabrics treated with manganese, 1.3% and 0.56%) shows that there is a continuous formation of reducing groups and that the rate at which they are further oxidized to carboxyl groups is slow.

The copper number represents the total reducing power of the cellulose molecule and includes reduction due to aldehydic groups in individual chains and reducing groups resulting from the oxidation of hydroxyl groups in glucose units. On theoretical grounds, the reduction due to aldehydic groups is small in comparison with that due to reducing groups

formed by the oxidation of hydroxyl groups. It would appear, therefore, that manganese protects the functional hydroxyl groups against oxidation, while metals like copper, tin and titanium, catalyse the reaction. Further work on the mechanism of protection is under way.

Acknowledgment

The authors offer their thanks to Dr. B. C. Bera and Messrs T. S. A. Padmanabhan, R. K. Verma, S. C. Katyar, R. S. Agarwal & N. K. Sen for technical assistance, and to the Director of Research and Development (General), Ministry of Defence, New Delhi for kind permission to publish the paper.

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Studies in Cellulose Chemistry : Part IV—Hydrated Oxides as Barriers Against Cellulose Degradation by Ultra-violet Irradiation

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The barrier effect of hydrated oxides of manganese, cobalt, nickel and copper as well as binary combinations of manganese-copper and nickel-copper have been investigated and some of the laboratory results compared with those of outdoor exposure trials. Hydrated oxides of manganese and nickel provide protection against cellulose degradation. Carboxymethyl derivatives of cellulose containing manganese, nickel and binary combination of manganese-copper have shown promise in laboratory trials.

The results of exposure trials carried out to investigate the barrier effect of hydrated oxides of various metals on cellulose against actinic degradation have been discussed in an earlier paper[1]. It was shown that while hydrated manganese oxide provided protection, hydrated oxides of copper accelerated degradation. The results of further attempts to improve the protective properties of manganese have been reported in this paper.

Since outdoor exposure trials are time-consuming, a Hanovia lamp[2] was used as the source of ultra-violet rays in laboratory trials. The barrier effect of hydrated oxides of manganese, cobalt, nickel and copper, as well as binary combinations of manganese-copper and nickel-copper have been investigated. Carboxymethyl derivatives of cellulose, containing these metals have also been prepared and tested in the laboratory. The results have been compared with the behaviour of fabrics treated with mineral khaki.

Experimental Procedure

The fabric used in the various trials was highly scoured cotton *dosooti*, weighing 7 oz./sq. yd.[2, 3].

Treatment of fabric—The general technique employed for treating the fabrics with various hydrated metallic oxidies was the same as that described in the earlier paper[2].

Mineral khaki—A 30 per cent solution of sodium dichromate in sulphuric acid was reduced by *gur* and when the reduction was complete, the density of the solution was adjusted to 24° Bé by dilution with water. Ferrous sulphate solution (12% by vol., 20° Bé was added and the fabric padded in the solution using a double three bowl padding mangle, adjusted for 80 per cent take-up. The padded fabric was dried in a hot air chamber at 83°C. for 15 min., and developed at boil in an alkali solution containing : caustic soda, 6.8 ; soda ash, 1.6 ; and sodium dichromate 0.5 per cent, on a jigger giving 8 ends. The fabric was then washed, soaped, washed again and finally dried.

Carboxymethylated derivatives—The fabric was steeped in monochloroacetic acid (30%) for 20 min., hydro-extracted and subsequently steeped in caustic soda (40% soln.) for 20 min. It was then removed and left for ageing in air for 45 min., and then washed in water free from alkali. A substitution amounting to one carboxymethyl group for every 22 anhydroglucose residues of the cellulose chain was obtained. When the sodium carboxymethyl derivative was steeped in a solution of manganese sulphate ($MnSO_4.4H_2O$, 2.5%), nickel sulphate ($NiSO_4.7H_2O$, 1.25%) and copper sulphate ($CuSO_45H_2O$, 1.6%) the respective metal derivatives were formed.

Exposure—A Hanovia Alpine Mercury Arc Sun lamp was used for irradiation[1]. Exposure was effected by keeping the fabric at a distance of 30 cm. from the lamp. A continuous stream of air was directed on the fabric during the irradiation in order to prevent any temperature rise.

In some cases, treated fabrics were exposed to sunlight according to the procedure previously described[1].

Assessment of degradation—The extent of degradation suffered by the fabric was assessed by measuring the loss in breaking strength. Samples were conditioned at 21°C. and 65–70 per cent RH for 48 hr., placed in a cloth testing machine and broken warpwise (distance between grips, 2 in. × $6\frac{5}{8}$ in.) under a constant stretch of 18 in./min.

Results and Discussion

The results obtained are given in Tables 1 and 2. The results show that besides manganese, nickel and cobalt also behave as actinic barriers. The protective action of nickel has been confirmed by outdoor exposure trials.

Copper does not accelerate the degradation of cellulose when exposed to ultra-violet light. This is in accordance with the results reported by Bartlett and Goll[5] that copper naphthenate does not catalyse the oxidation of cellulose when exposed to a fadeometer.

Binary combination of copper with manganese or nickel reduces the loss in strength much more than copper. However, it may be observed that

the best protection is offered by mineral khaki (Table 1). In outdoor exposure to sunlight, however, the performance of mineral khaki was no better than that of the fabric protected by manganese. The results obtained with copper in outdoor trials are rather anomalous. While, according to laboratory trials, copper treatment afforded some degree of

TABLE 1—BARRIER EFFECT OF METALLIC HYDROXIDES AGAINST ULTRA-VIOLET IRRADIATION

Metal concentration %	Laboratory irradiation		Outdoor exposure	
	Exposure period *hr.*	Loss in breaking strength %	Exposure period *hr.*	Loss in breaking strength %
Manganese (0.60)	72	29	2,400	13
Cobalt (0.73)	48	18	..	..
Nickel (0.20)	72	26	2,100	22
Copper (0.50)	72	37	1,200	100
Manganese (0.60) + Copper (0.50)	72	25	..	..
Nickel (0.20) + Copper (0.52)	72	25	..	..
Mineral Khaki (Fe. 0.80; Cr. 2.80)	72	9	2,400	12
Untreated Control	72	47	2,400	65

TABLE 2—PROTECTIVE EFFECT OF METALLIC DERIVATIVE OF CARBOXYMETHYL CELLULOSE

(*Exposure period, 48 hr.*)

Metal concentration %	Breaking strength loss %
Sodium ..	54
Managenese (0.65)	20
Nickel (0.25)	30
Copper (0.40)	43
Copper (0.40) + Manganese (0.60)	31
Untreated Control	42

protection to fabrics the results of outdoor exposure to sunlight, show that copper treatment accelerated deterioration.

Carboxymethyl derivatives—Among the carboxymethyl derivatives (Table 2), those of manganese, nickel, and binary combination of copper-manganese provide some protection against deterioration when exposed to ultra-violet light. Copper does not provide any protection and the sodium derivative accelerated cellulose degradation.

Acknowledgment

Thanks are due to the Director of Research and Development (General), Ministry of Defence, New Delhi, for kind permission to publish the paper.

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Reactions of Cellulose with Cross Linking Agents

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Recent advances in the chemistry of cross linking reactions and their application in the textile industry have been reviewed. Particular reference has been made to the applications of urea-formaldehyde and melamine-formaldehyde condensation products in imparting dimensional stability and crease-resistance to cotton and viscose textiles.

Cellulose consists of long chains of glucopyranose residues linked through 1 : 4 β-glucosidic bonds. These chains are close packed with some degree of order in the so-called crystalline regions, whereas in non-crystalline regions, the glucopyranose residues are present in a more or less disoriented arrangement. Along the b-axis, the chains are held together, forming a sort of laminae or micelles, by hydrogen bonds, which are most likely to be formed in the more orderly crystalline regions. Along the c-axis, there are only weak Van der Waals forces between the laminae.

A certain degree of confusion exists in the use of the terms 'amorphous', 'crystalline', 'accessible' and 'inaccessible' regions, and values obtained for these by different authors vary according to the methods used for their measurement. There is also some confusion in the notations for the axes. Whereas crystallographers call the fibre axis or the axis along the length of the molecular chains as b-axis, physicists and chemists call this the a-axis. In spite of all this, cellulose can be described as a three-dimensional polymer, in which there are strong covalent β-glucosidic bonds along the a-axis, hydrogen bonds along the b-axis and weak Van der Waals forces along the c-axis, and in which the long chains of glucose anhydride units are arranged in different degrees of order and disorder in different portions of the macromolecule. Cotton and viscose both have the same basic structure; they differ, however, mainly in their average degree of polymerization and the amount of amorphous or accessible region. Thus while cotton has a degree of polymerization (D.P.) of *c.* 3,000 with 15 to 30 per cent accessible region, viscose has a D.P. of 400–500 and has 50 to 60 per cent of accessible region.

The two main weaknesses of cellulosic textiles, namely, poor dimensional stability in wet treatments and ease of creasing, can be understood on the

basis of the structure of cellulose. When cellulose is treated with water or other aqueous solution, they enter into the accessible region and produce cross-sectional swelling by overcoming the weak hydrogen bonds and Van-der Walls forces along the b- and c-axis. It can be easily seen that such a swelling of fibres in a yarn would result in longitudinal shrinkage due to constraints placed on the fibres by the yarn twist. Similarly, cross-sectional swelling of yarn in a fabric results in a shrinkage along the length and width.

When a tensile stress is increasingly applied to a cellulosic fibre, the weak hydrogen bonds between molecular chains are easily broken producing slippage of one chain against another till the fibre ruptures. Thus, in the stress-strain behaviour of these fibres, there is, at relatively low strains, a large area of plastic flow or time-dependent creep, where the extension produced is non-recoverable. This poor elastic performance is responsible for the easy creasing of cotton and rayon fabrics.

In order to reduce water-imbibition and improve crease recovery, attempts have been made to introduce covalent cross bonds between glucose residues on neighbouring chains of the cellulose molecule. Since the early attempts of Eschalier[1] and, a little later, of Cross and Bevan[2], to improve the wet strength of rayon by treatment with formaldehyde and acetic or lactic acid, followed by drying at 40–50°C., considerable progress has been made, and many reagents have been used to cross link cellulose. However, it is only in recent years that we have obtained some understanding of the mechanism of simple cross linking reactions, such as that of cellulose with formaldehyde. It would not be out of place to review, in some detail, the significant results reported in this field.

Meunier and Guyot[3] postulated that methylene bridges, $-O-CH_2-O-$, are formed by formaldehyde with two glucose residues of cellulose. Wood[4] disagreed with this postulate and suggested that methylene bridges were formed on two hydroxyls of the same glucose residue or, alternatively, that hydroxy-methyl groups, $R-O-CH_2-OH$, were formed in the hydroxyls of cellulose. According to Schenk[5], the changes brought about by formaldehyde in the properties of cellulose can be explained by the formation of cross links between two adjacent cellulose molecular chains. Dillenius[6] also arrived at the same conclusion from a review of earlier work.

Most recently, Gruntfest and Gagliardi[7] observed that cellulose (ZOH) can react with formaldehyde in the following possible ways :

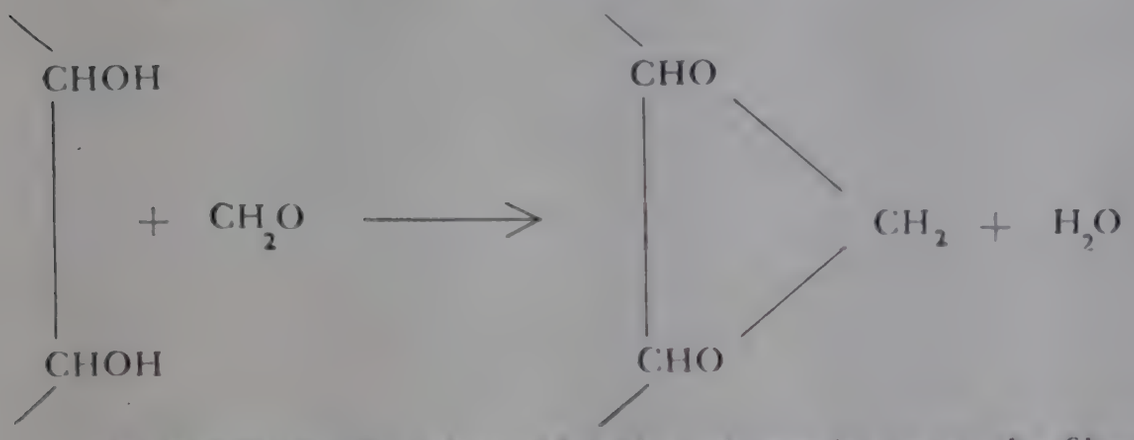
(1) $ZOH + CH_2O \longrightarrow ZOCH_2OH$

(2) $2ZOH + CH_2O \longrightarrow ZOCH_2OZ + H_2O$

(3) $ZOH + n(CH_2O) \longrightarrow ZO(CH_2O)nH$

(4) $2ZOH + n(CH_2O) \longrightarrow ZO(CH_2O)nZ + H_2O$

(5) Ring closure by reaction of formaldehyde with two hydroxyl groups of the same anhydro glucose unit :



(6) Deposition of a formaldehyde polymer in or on the fibres.

Reaction 5 is not very likely to occur, since it involves the formation of a 3-membered ring. Reactions 1 and 3 involve the formation of hydroxymethyl groups without any loss of water. Reactions 2 and 4, on the other hand, lead to the formation of ethers with removal of one molecule of water and give products which are stable to hydrolysis. In reaction 6 also, there is no loss of water. Again, the combining weight of formaldehyde will be 30 in reaction 1 and multiples of 30 in reaction 3, depending on the value of n. On the other hand, the combining weight of formaldehyde in reaction 2 is only 12, whereas in reaction 4, it is 21, 24 and 25.2 respectively, for n=2, 3 and 4.

Gruntfest and Gagliardi used experimental data on material balance, amount of fixed formaldehyde and combining weight of formaldehyde to study the mode of reaction.

When rayon was treated with 20 per cent formaldehyde and different concentrations of hydrochloric acid catalyst, approximately equal weight gains were obtained after curing. However, on boiling with water, there was a loss in weight of products cured with lower acid concentrations, while there was an increase in weight of products cured with higher acid concentrations. Similar results were obtained by using catalysts of widely varying acidities. This suggests that there is a substantial change in the nature of the product of cellulose-formaldehyde reaction as the acidity of the catalyst increases. It is likely that under alkaline or weakly acid conditions of curing, reactions 1, 3 and 6 take place. Under strongly acidic conditions of curing, reactions 2 and 4 are more probable.

The combining weight of formaldehyde varies with its concentration in cellulose. At lower concentrations, the combining weight approaches a value of 12, corresponding to the formation of simple methylene ethers as in reaction 2. At higher concentrations, the combining weight increases and ethers of the type Z-O $(CH_2O)_n$-Z are probably formed according to reaction 4.

Reduced water-imbibition, insolubility in cellulose solvents and increased fibre stiffness and elastic recovery also point to the formation of cross links.

Wagner and Pacsu[8] used a different approach in the study of the cellulose formaldehyde reaction. They argued that if some of the hydroxyls of cellulose were involved in cross link formation, this should be reflected in the results of methylation and methanolysis of the methylated product, and in such reactions as periodate oxidation. By reacting acid-treated cotton with formaldehyde in the vapour phase at 110–150°C. for 1-24 hr., they obtained a fixed formaldehyde content of 5 per cent or more. Methylation of the product gave a methoxyl content of *c.* 32 per cent against 43 per cent methoxyl for untreated native cellulose. If each molecule of formaldehyde reacts with two, and only two, hydroxyls in cellulose and complete methylation of all residual free hydroxyls was obtained, the theoretical methoxyl content of the product should have been 37.2 per cent. This was a definite evidence that the reaction occurred between monomeric formaldehyde and two cellulose hydroxyl groups, and that the fixed formaldehyde was covalently bonded to the cellulose molecule.

Methanolysis of methylated formaldehyde-reacted cellulose gave 39.1 per cent of 2,3,6-trimethyl glucoside, 31.9 per cent dimethyl methyl glucoside and 29.0 per cent monomethyl methyl glucoside. The dimethyl derivative represents the fraction of glucose residues in which one hydroxyl is involved in a methylene bridge, while the monomethyl derivative represents those glucose residues in which one hydroxyl is involved in a methylene bridge and the bridge inhibits the methylation of an adjacent hydroxyl. The yield of trimethyl methyl glucoside agrees well with the assumption that each molecule of formaldehyde substitutes two, and only two, hydroxyl groups. The complete absence of 2,3-dimethyl methyl glucoside shows that the primary hydroxyl groups are not involved in methylene bridges. This was further confirmed by the results of periodate oxidation; periodic acid consumption was much lower for formaldehyde treated cellulose than for natural cellulose.

Karrholm[9] studied the changes in bending, torsion and stretching moduli as the amount of formaldehyde (both fixed and soluble) in viscose rayon was increased. It was observed that all three moduli increased with increase of formaldehyde, passed through a maximum at 5–7 per cent formaldehyde content, and then decreased (Figs. 1 and 2). If one molecule of formaldehyde reacts with two hydroxyl groups in different glucose units, the maximum amount of formaldehyde in the fibre would be:

$$\frac{30\times100}{2\times162}=9.3\%$$

If the reaction is confined to the amorphous parts only, the maximum would be approximately $9.3\times0.6=5.6$ per cent. If was concluded

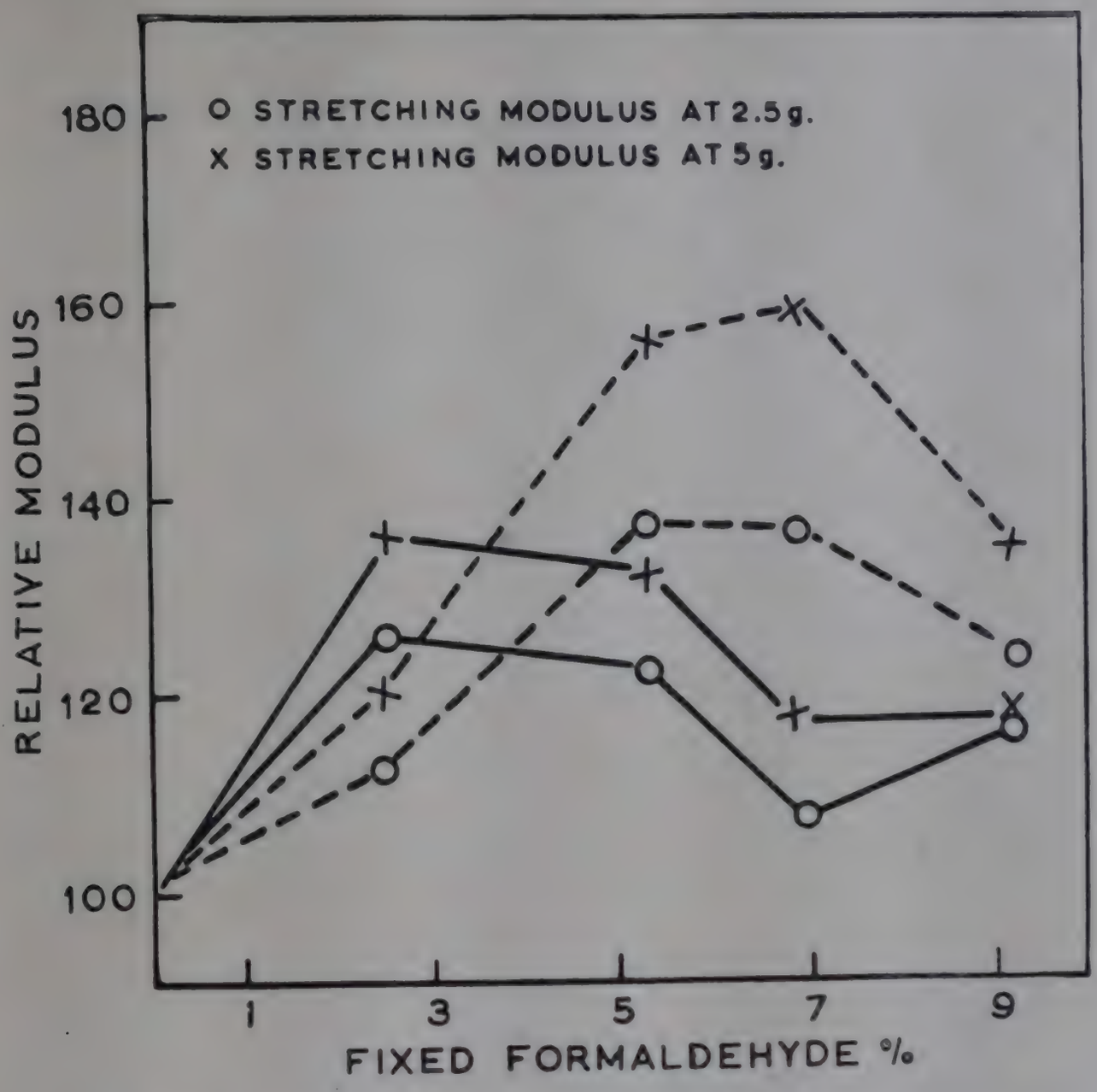


FIG. 1—CHANGES IN STRETCHING MODULUS WITH INCREASE IN FORMALDEHYDE CONCENTRATION

that as the concentration of formaldehyde is increased, an increasing number of short cross links is formed giving an increase in the moduli up to *c.* 5 per cent fixed formaldehyde. When the fixed formaldehyde is 7 per cent, some of the cross links are longer, consisting of two or more formaldehyde molecules, producing a decrease in the moduli. The moduli decreases further as the fixed formaldehyde increases to *c.* 9 per cent, when most of the cross links probably contain on an average two formaldehyde molecules.

Formaldehyde treatment confers dimensional stability, crease-resistance and reduced water-imbibition to cotton and rayon materials. However, the acid catalysed reaction also causes cellulose degradation and brittleness. Various alternative methods[10] have been tried to produce cross bonding : some of them are mentioned here. Glyoxal reacts readily with viscose in the presence of an acid catalyst. The reaction is analogous to that with formaldehyde and the probable cross bonds formed are :

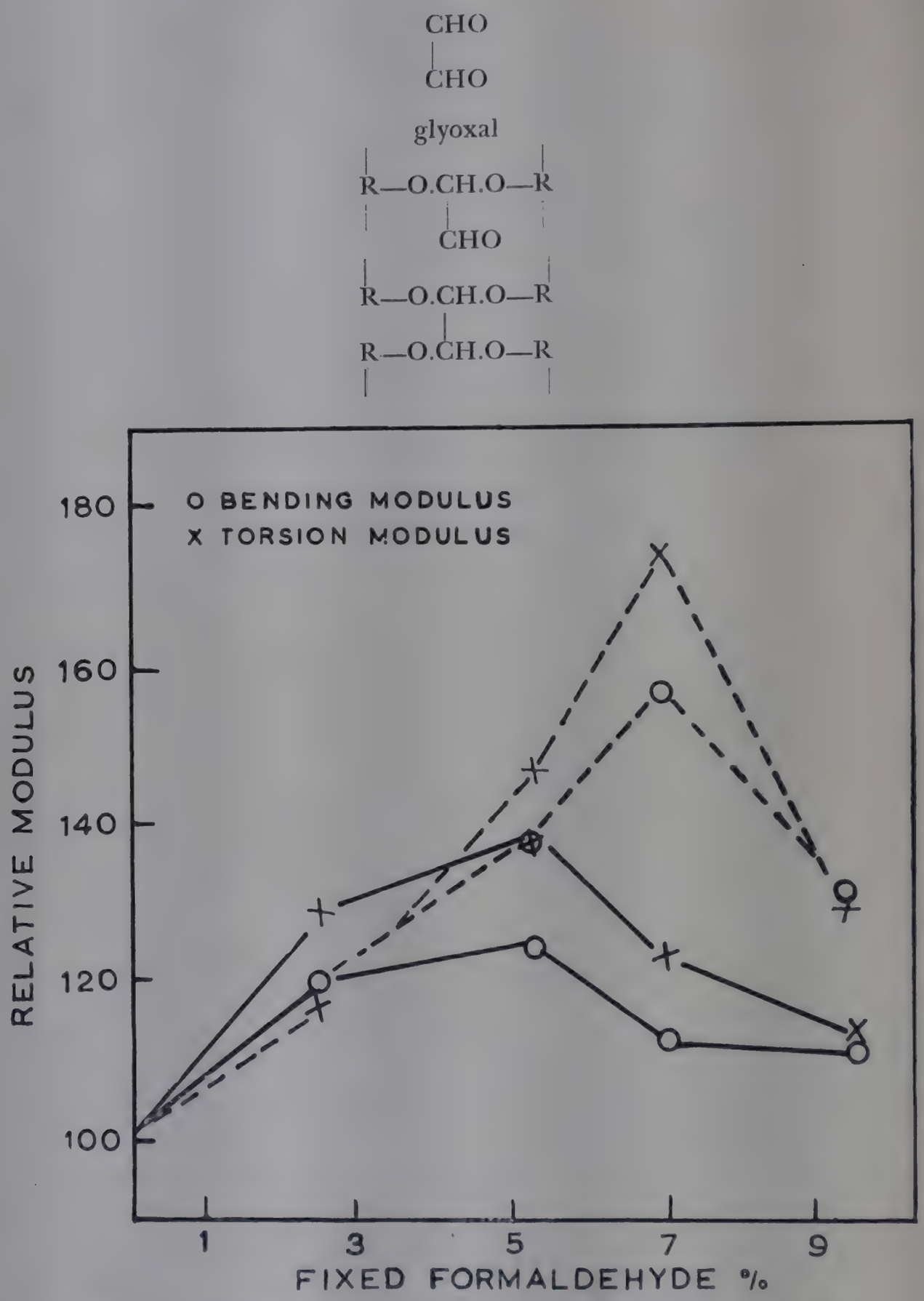
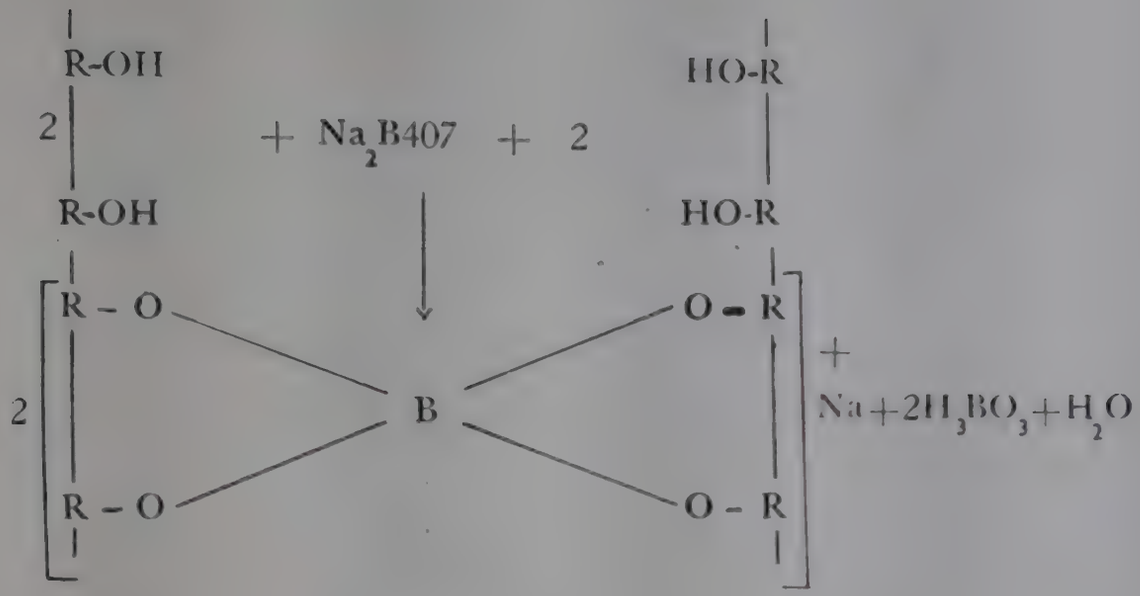


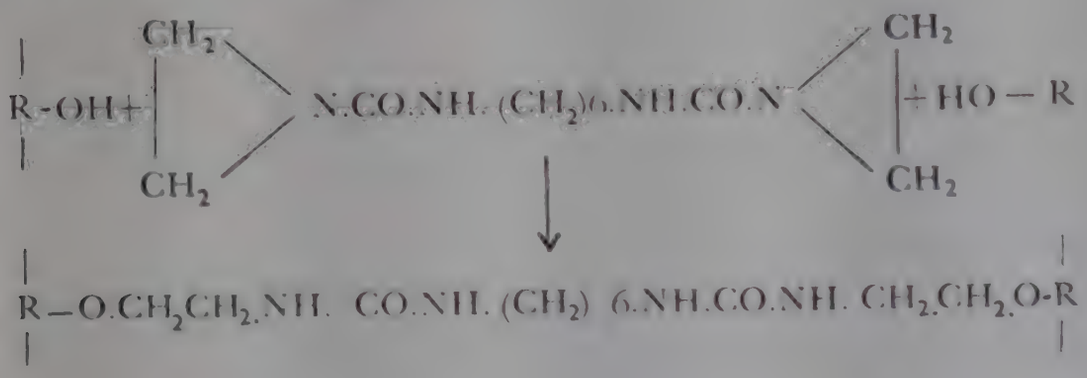
FIG. 2—CHANGES IN BENDING & TORSION MODULI WITH INCREASE IN FORMALDEHYDE CONCENTRATION

Borax also forms cross bonds with viscose cellulose. The bonds are, however, different in that co-ordination complexes, not covalent links, are formed.

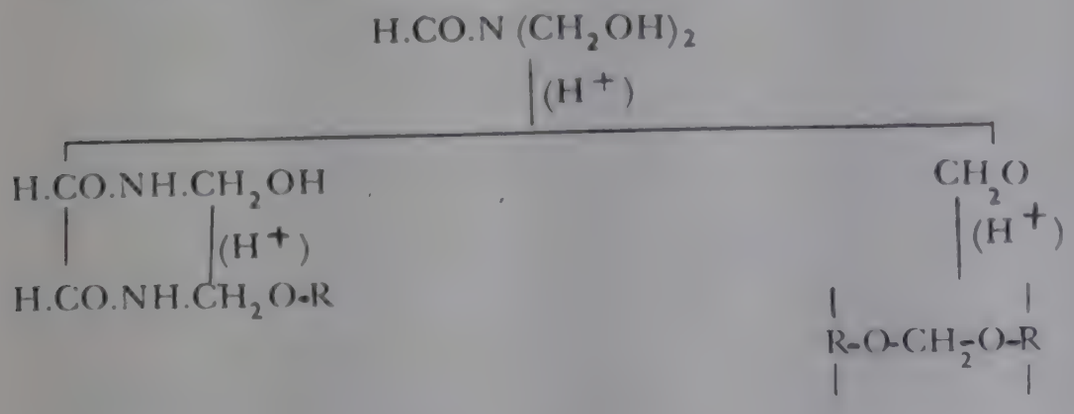


The energy of this bond is 10—20 kg. cal. as compared to 80—100 kg. cal. for a covalent bond. The bond is broken by water and by chemical treatment.

Derivatives of ethylene urea, produced by the interaction of ethyleneimine and an isocyanate, are also capable of producing cross bonds. The reaction occurs at comparatively low temperatures (100–120°C.) without a catalyst, according to the following mechanism :

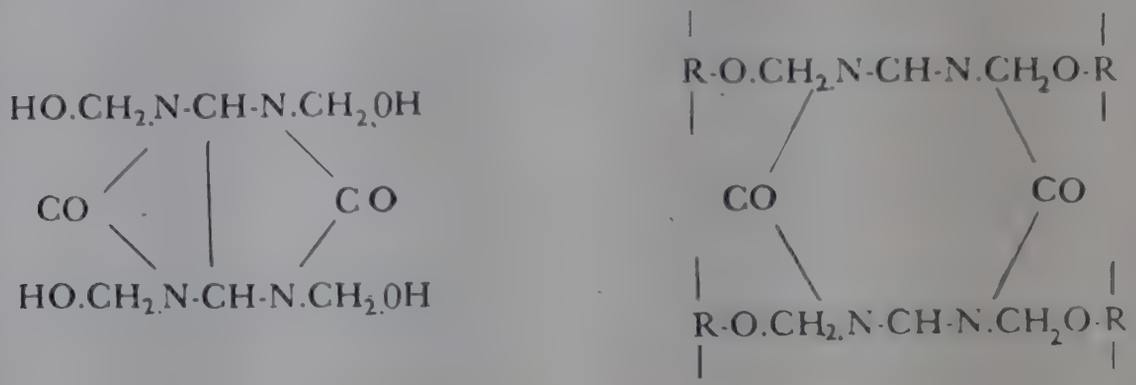


Dimethylol formamide also forms cross bonds with viscose in the presence of an acid catalyst. The reaction is as follows :

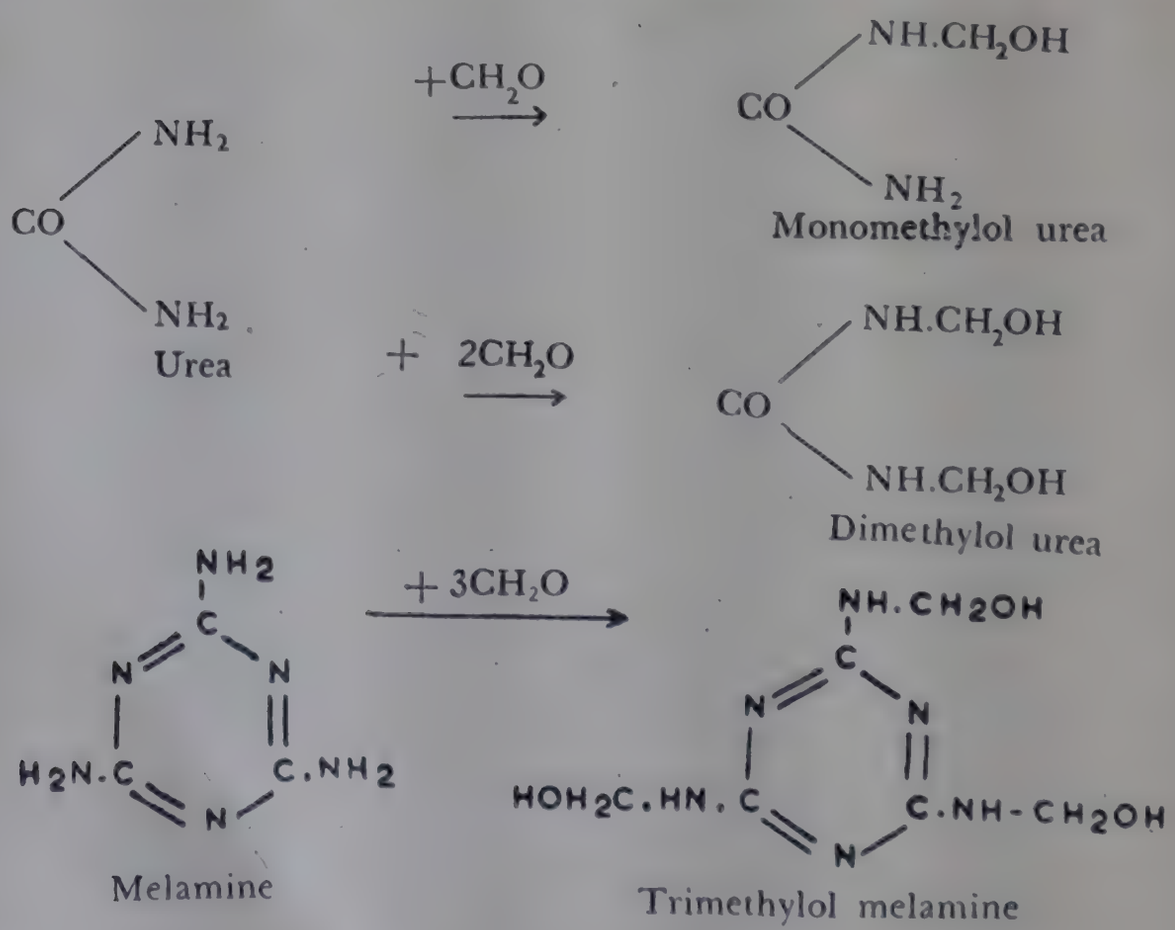


Dimethylol formamide liberates formaldehyde and forms ether links, its residue being attached to the cellulose at the end of the reaction to give the formamido-methyl ether.

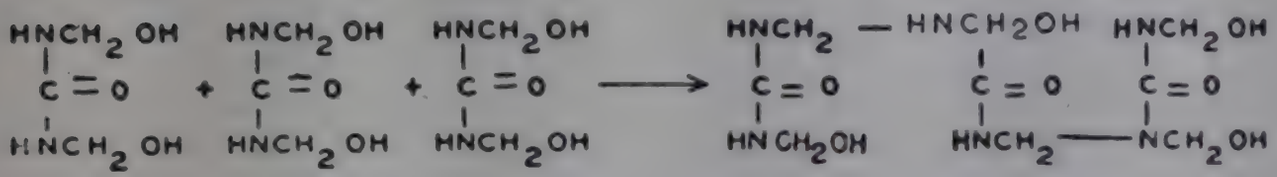
The compound produced by the reaction of formaldehyde with the condensation products of glyoxal and urea reacts with viscose in the presence of an acid catalyst to give cross bonds as follows :



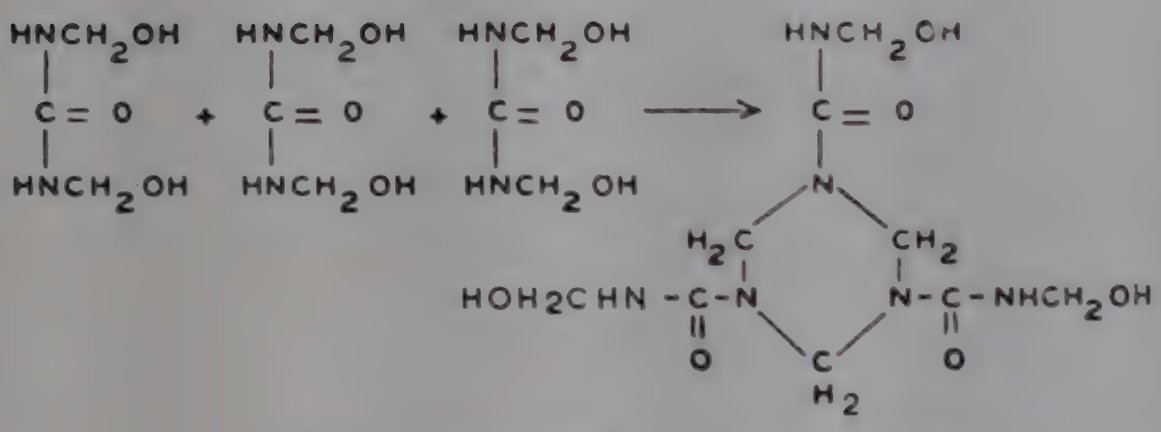
From the industrial point of view, the most significant advance over the simple cellulose-formaldehyde reaction is the application of urea-formaldehyde and melamine-formaldehyde condensation products to cotton and viscose cellulose. Under alkaline conditions, urea and melamine react with formaldehyde to give the following water-soluble crystalline products :



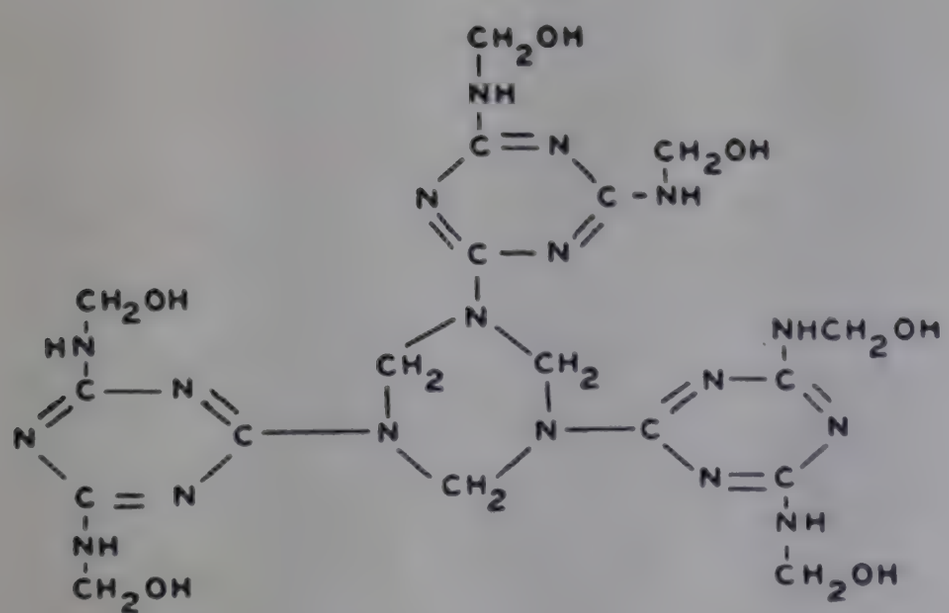
Under acidic conditions, these simple compounds rapidly polymerize with increasing viscosity and decreasing water solubility, giving in the end a hard, amorphous, infusible mass of resin. Polymerization occurs in many complex ways, two of which are shown below.



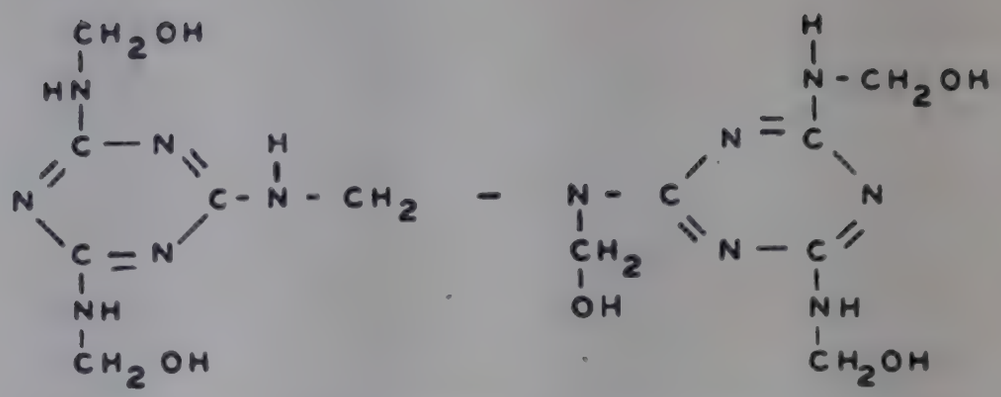
Urea formaldehyde polymer, linear type



Urea formaldehyde polymer, cyclic type

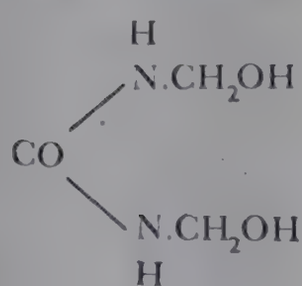


Melamine formaldehyde polymer, linear type



Melamine formaldehyde polymer, cyclic type

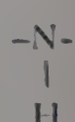
This is a simple picture of what happens in the commercial process, where the water-soluble crystalline products mentioned earlier are applied to the cotton or viscose material in presence of an acidic or potentially acidic catalyst, followed by drying and baking at an elevated temperature. The chemistry of the reactions involved in resin treatment is, however, complex and even after 25 years of industrial use of the process, there is still a lively controversy as to whether the reaction involves cross linking with cellulose or merely an interstitial deposition of the resin polymer. It has been well established that the resin monomer penetrates into the accessible regions of the fibre. The pore size of the cotton fibres has been shown, from low temperature gas sorption data, to be 16—20 A. Compared to that, the largest dimension of monomeric trimethylol melamine is only 12.7 A., while the urea-formaldehyde monomer is much smaller[11]. The resin monomer can, however, react with the cellulose in a large number of complex ways. Consider, for example, a simple reagent like dimethylol area. Its basic reactions are as follows[12] :



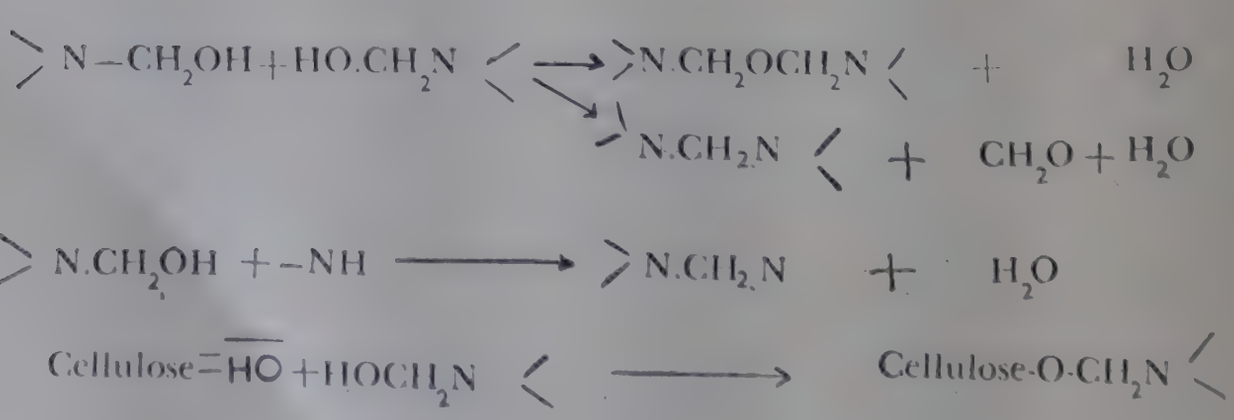
Dimethylol urea

Reactive Groups

N-Methylol

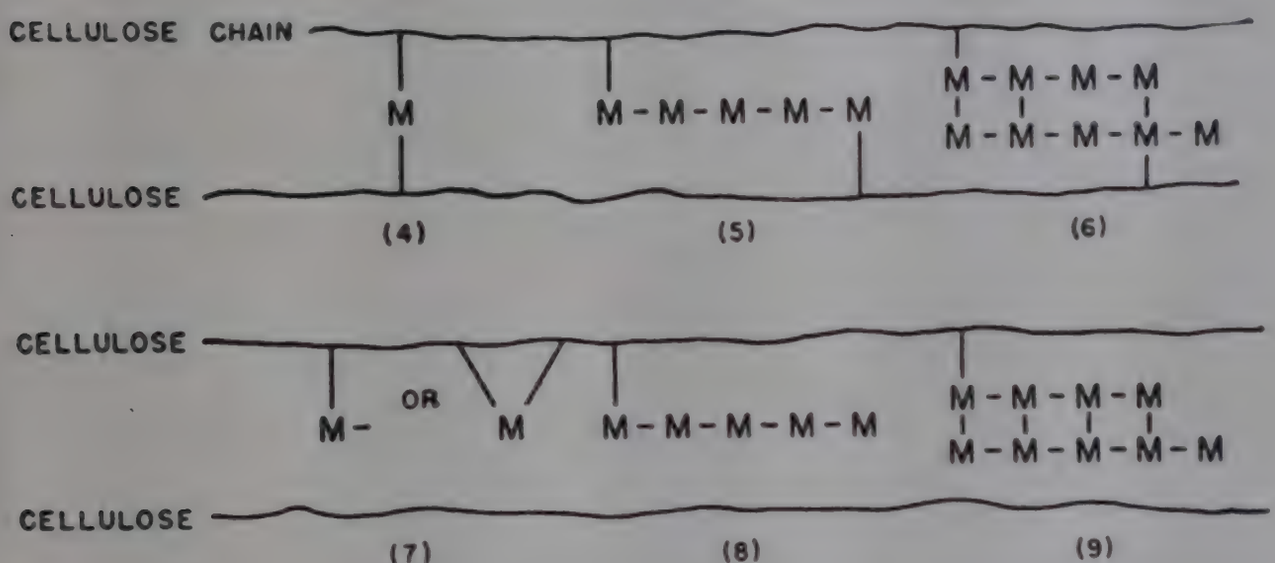


Imido



From these basic reactions, at least nine different reactions are possible under curing conditions[12] as follows (M represents dimethylol urea) :

1. Cyclic dimer
2. Linear polymer
3. Thermoset polymer
4. Simple cross link
5. Linear polymer, cross linked to cellulose
6. Thermoset polymer, cross linked to cellulose
7. Monomer linked to only one cellulose chain
8. Linear polymer, linked to only one cellulose chain
9. Thermoset polymer, linked to only one cellulose chain



The conditions of curing are such that both cross linking and resin formation are equally likely to occur.

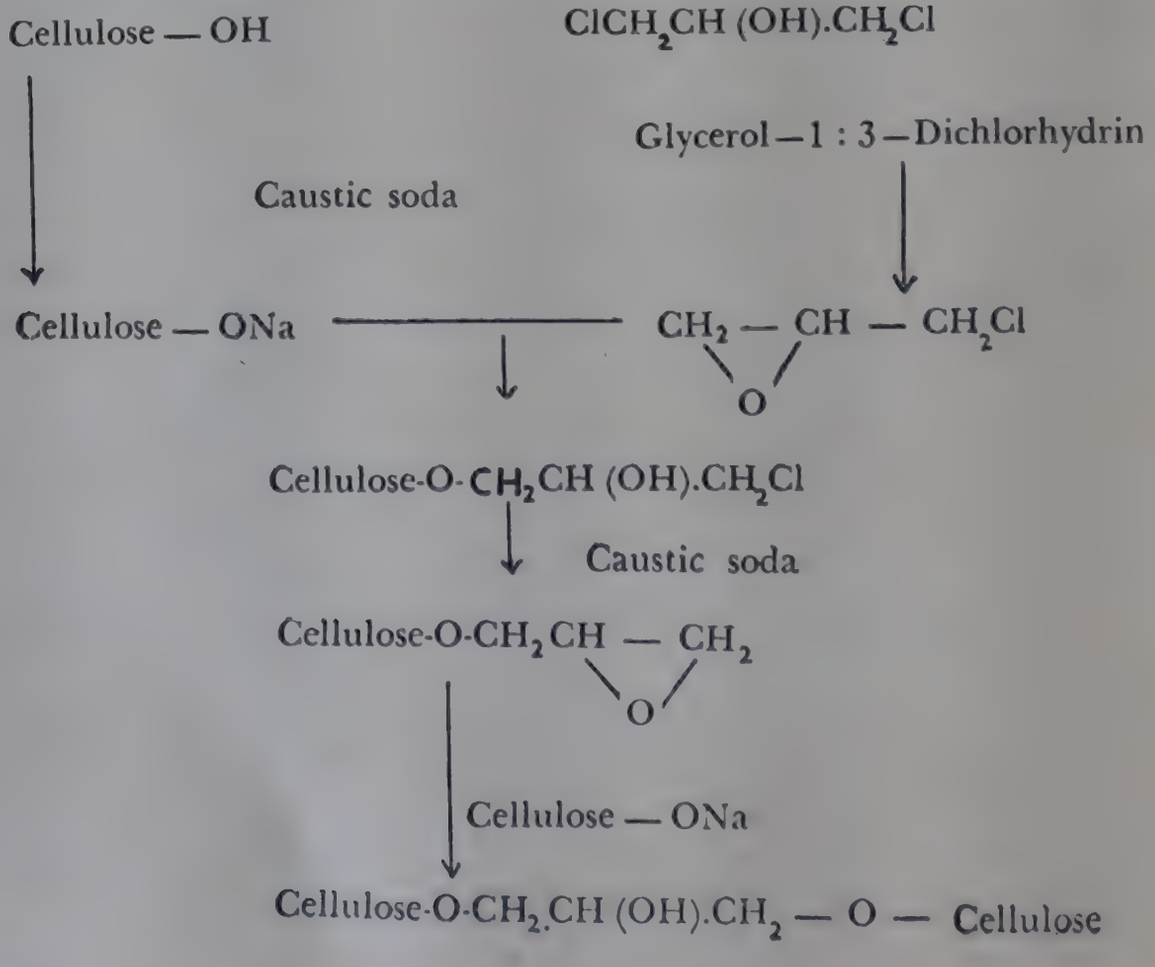
It has been shown that the elasticity of the fibre is improved and its extensibility decreased as a result of such resin treatments[13]. It has also been shown that these changes in the fibre properties are largely responsible for the improved crease-recovery and reduced tear strength and abrasion resistance of the treated cotton fabrics. Increased elasticity, reduced water sorption and insolubility in the usual cellulose solvents have been advanced as evidence for the formation of cross links. However, no direct chemical evidence is available for the existence of cross links as in the case of the cellulose-formaldehyde reaction.

The two major defects of fabrics treated with these resins are : development of a fishy odour and chlorine retention. The former has been traced to the formation of methylamines from the reaction of formaldehyde with the ammonium salt catalyst and its decomposition products in the curing operation. The use of non-ammoniacal catalysts, such as organic amine-hydrochlorides and inorganic salts, or the use of formaldehyde acceptors, such as urea, eliminates odour formation. Chlorine retention of the resin-treated cellulose is due to the presence of primary and secondary amine groups in the nitrogenous resins, which

pick up chlorine from hypochlorite bath and form chloramines. The chloramines decompose at high temperatures liberating free hydrochloric acid, which produces yellowing and degradation of cellulosic material. Modified resins, in which all the H atoms of the amine groups are substituted, cause much less chlorine retention. Examples of such resins are dimethylol ethylene urea and methylated methylol melamine.

To avoid the danger of chlorine retention in resin-treated cellulosic materials, a new finishing process has been evolved, in which a condensation product of acetone and starch-methylol is applied to the fabric, in the presence of an alkaline catalyst, followed by drying and curing at high temperature. It is likely that in the curing stage, the long chain cellulose molecules become cross linked through the acetone-starch-formaldehyde condensation product. The well-known 'Aviscoset' finish for viscose rayon fabrics is closely related to this process, the essential difference being that starch is replaced by a water-insoluble, alkali-soluble cellulose ether, such as a hydroxyethyl cellulose ether.

An interesting finishing process, devised to produce cross linking, uses a special type of halogenated aliphatic or alicyclic compound, such as glycerol-1 : 3-dichlorhydrin, in which there are at least two halogen atoms on different C atoms, both capable of forming epoxide rings with at least one hydroxyl group also present in the molecule[14]. The reaction, which is complete in a few minutes at 90°C. in the presence of an alkali catalyst, is believed to occur in the following stages :



Finally, mention must be made of a recent development, which uses di- and poly-isocyanates instead of formaldehyde for the finishing of textile[14] materials. For example, hexamethylene di-isocyanate, obtained by the reaction of hexamethylene diamine and phosgene, reacts with cellulose to give a urethane type of cross bond. For commercially useful results, a fairly long carbon chain between the terminal isocyanate radicals is found necessary. *m*-Phenylene di-isocyanate, toluene-2:4-di-isocyanate, toluene-2:4:6-tri-isocyanate and similar poly-isothiocyanates can be used to produce cross links in cellulose. All the compounds hydrolyse in water and must be used in organic solvents.

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Discussion

Dr. P. K. Choudhury: Is there any positive evidence of the linkage of resin with cellulose? Is there any difference in X-ray diffraction of resin-treated and untreated cellulose?

Dr. P. C. Mehta: There is no direct evidence available regarding the linkage of cellulose and resin. The changes in mechanical properties have been taken as indirect evidence of cross linking.

Dr. T. Radhakrishnan: X-ray diffraction of resins is low, but the introduction of a heavy metal in the resin structure may give sufficiently intense X-ray diffraction and provide information on the distribution of resin in cellulose.

Dr. P. K. Choudhury: Has any work been done to show whether primary hydroxyl groups are involved in the reaction between resins and cellulose?

Dr. P. C. Mehta: As far as I know, no work has been done.

Shri G. M. Vyas: We have found that properties of papers obtained from wet pulp and dry pulp are different. Is there any possibility of cross linking?

Dr. P. K. Choudhury: Only physical changes are likely to occur during drying, producing hydrogen bonds.

Shri G. M. Vyas: Can viscosity determination give any clue ?

DR. P. C. MEHTA: Cross linked cellulose is not soluble in cuprammonium hydroxide and acidic solvents will hydrolyse cross links.

DR. A. B. SEN GUPTA: Can you study the location of resin by microscopic techniques?

DR. P. C. MEHTA: You can know whether the resin is inside or outside the fibre by well-known staining techniques, but the manner of distribution of resin inside the fibre cannot be known.

SHRI R. G. MANUDHANE: Can one use alkaline catalysts with urea and melamine resins?

DR. P. C. MEHTA: Gagliardi has used alkaline catalysts. With these catalysts there is no possibility of cross linking. However, we have noticed in our experiments, yellowing with alkaline catalysts.

SHRI R. J. CHIKTE: What is the reason for loss in tensile strength of resin-treated cellulose?

DR. P. C. MEHTA: Changes in mechanical properties can all be explained by the increased elasticity and the reduced extensibility of treated fibre.

SHRI R. J. CHIKTE: Are there any means to reduce the strength loss?

DR. P. C. MEHTA: Three different approaches have been used to achieve this, namely, (i) proper fabric construction, (ii) use of appropriate softeners, and (iii) altering the nature and distribution of resin in the fibre.

Chemical Modification of Textile Celluloses

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Shri Ram Institute for Industrial Research, Delhi

The structure of cellulose as a linear polymer exhibiting properties akin to polyalcohol compounds has been briefly reviewed. It is pointed out that the characteristic alignment of chain molecules, resulting in close and orderly packed 'crystalline' regions and disorderly packed 'amorphous' regions is responsible for many of the textile properties, such as tensile strength, elasticity, dye-receptivity, moisture regain, etc. Such textile properties are separately classified on the basis of their relation with cellulose structure. An attempt has been made to outline the various chemical modifications that could be brought about with a view to improving one or more of them.

Cotton cellulose is a linear polymer containing hundreds of interlinked glucose units through oxygen bridges. It contains both primary alcoholic groups (CH_2OH) and secondary ones (CHOH), and from the chemical point of view, one would expect cellulose to behave like alcoholic compounds. However, when one thinks of cellulose from the point of view of textile end use, he is confronted with a number of limitations. Such limitations arise out of the necessity to maintain practically all the textile properties that cellulose normally possesses. For instance, the chemical treatment must not alter the tensile strength, which is believed to depend on chain length and intermolecular cohesion; secondly the treatment should not adversely affect the moisture relations of cellulose; thirdly the elastic properties which make spinning possible should not be destroyed; and lastly the treatment should affect useful textile properties, such as dye-ability, handle, drape, lustre and softness.

In the ultimate analysis, all the above limitations involve a thorough understanding of the physical structure and chemical properties of textile cellulose. Fortunately, thanks to the numerous pioneering researches conducted during the last fifty years or so, a fund of knowledge is now available which makes discussion possible. Modern fibre science has made great strides as a result of the impetus received through the synthesis of new chemical fibres. At one time it was considered that 'king cotton' will have to lose ground to modern synthetic fibres. But it was soon realized that, if starting from raw materials like coal tar or petroleum chemicals, which have no relation whatsoever with fibrous properties, one could synthesize such valuable fibres as

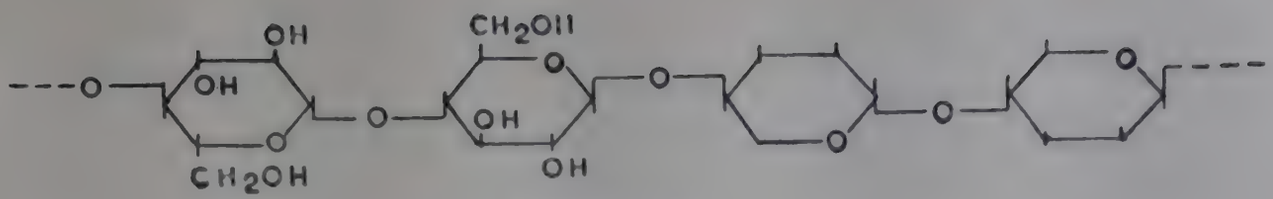
nylon or terelyne, one could as well start from cotton, flax, ramie, or jute and look forward to many and far reaching results. This view has gained considerable support during the last ten years [1-3].

Structure of Cellulose

All textile materials are linear polymers characterized by the presence of long chain molecules possessing polar side groups, such as OH, NH_2, etc., with residual valencies. The long chains are arranged in a remarkably orderly fashion and are held together by Van der Waals forces, hydrogen bonds or salt linkages between acidic and alkaline polar groups of adjacent molecules. In textile celluloses, the chain length varies from 300–600 glucose units (regenerated fibres) to 3,000–7,000 or more glucose units (natural celluloses). The cohesive forces between the side chains are due to hydrogen bonding between the hydroxyl groups of adjacent chains. In some places, along the length, these chains are packed together in a rather rigid and orderly fashion. These regions are called 'crystalline' regions and are believed to contribute mainly to the tensile strength and chemical stability. Further, these molecules are generally oriented towards the fibre axis. The degree of such orientation plays an important part in the tensile behaviour of cellulose. In other regions, the packing of molecules is not orderly; these regions known as 'amorphous' regions are believed to be more easily accessible to moisture, dyes and other chemicals. They may also account for the elasticity and extensibility of textile fibres.

The following points are worth recapitulating: (i) the chain length and degree of orientation contribute largely to the strength and other tensile properties of textile celluloses; (ii) the manner of random packing of molecules in the 'amorphous' regions of cellulose determines its accessibility to all outside chemical agencies. Chemicals having a molecular size greater than the molecular voids in the amorphous regions cannot enter them and hence cannot bring about easy chemical transformation; (iii) the alcoholic nature of polar hydroxyl groups in cellulose makes possible reaction between cellulose and alcoholic groups, resulting in reactions, such as etherification, esterification, xanthation, oxidation, etc., and (iv) chemicals having strong hydrogen bonding properties have an affinity for cellulose and can bring about changes in the physical properties of cellulose by altering the nature of packing of different chains (mercerization) or by clinging on to them and then adding to themselves until the size of the agglomerate becomes so big that a removal, by reversal, of the effect is made difficult.

These ideas can be made clear by reference to Figs. 1 and 2, which show the unit residue from which cellulose is built, the manner in which molecular chains cohere in the fibre and the manner in which they are packed.



CELLULOSE

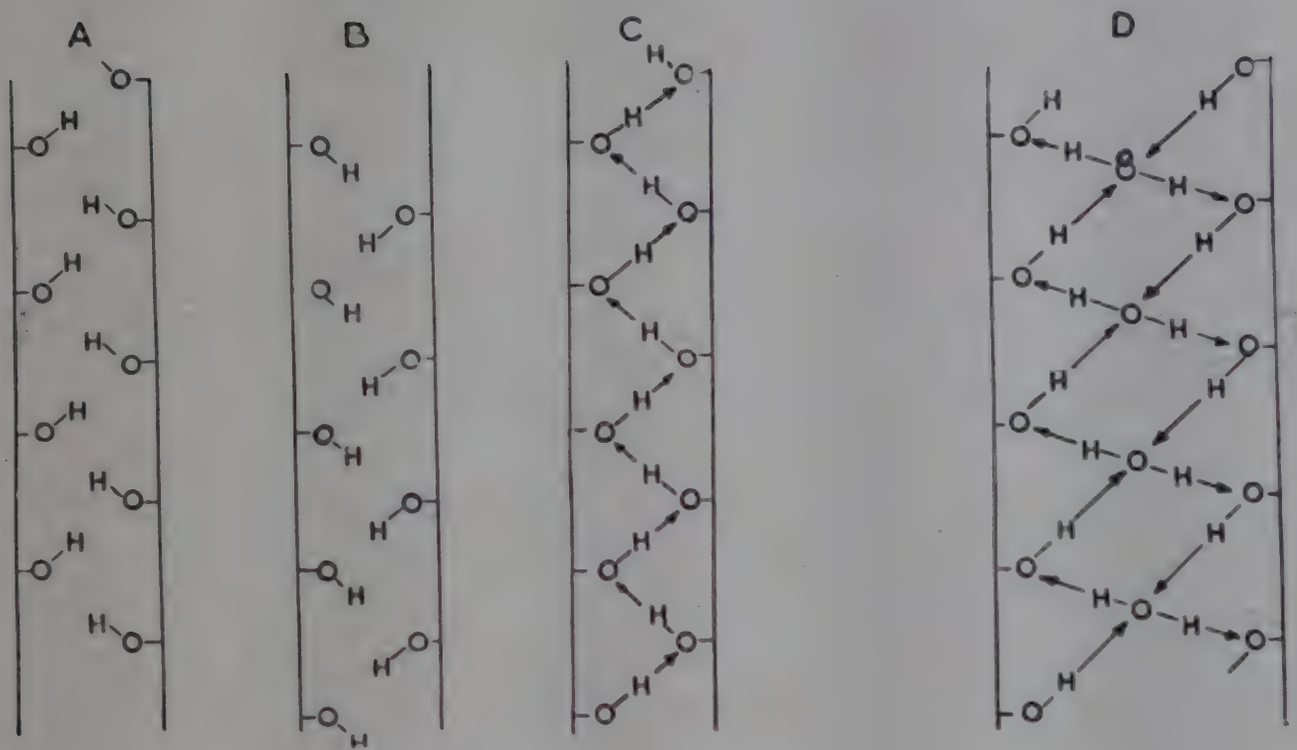
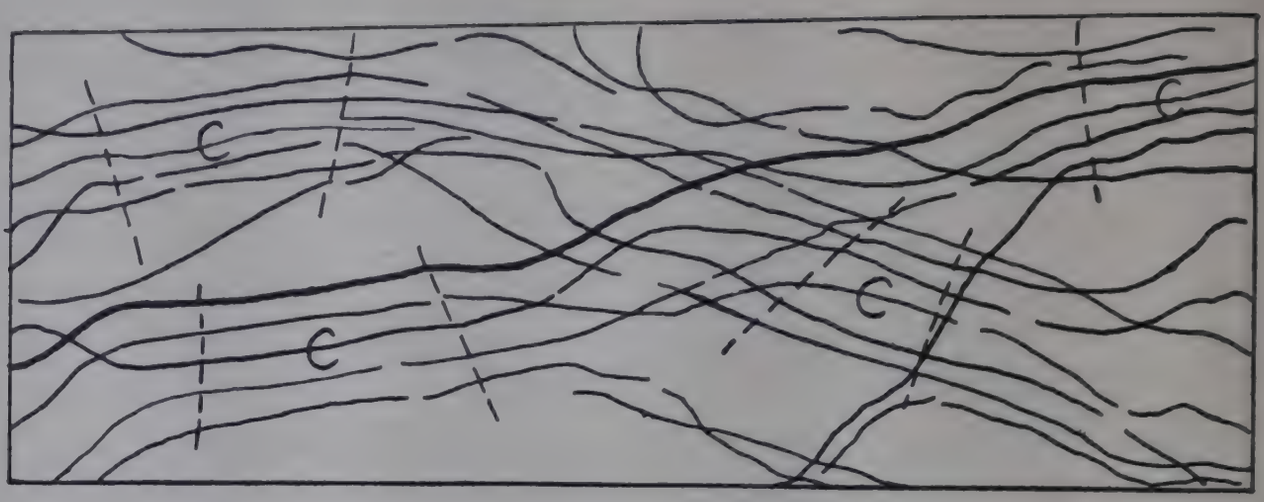


FIG. 1—CELLULOSE UNIT RESIDUE AND MOLECULAR CHAINS—A & B, SPATIAL DISTRIBUTION OF OH GROUPS; C, HYDROGEN BONDING THE OH GROUPS; D, INTENSITY OF HYDROGEN BONDING IN THE PRESENCE OF WATER [NATIVE CELLULOSE D.P. 5,000 (MOL. WT. 800,000); COMMERCIAL CELLULOSE D.P. 100–600 (MOL. WT. 10,000–96,000)]

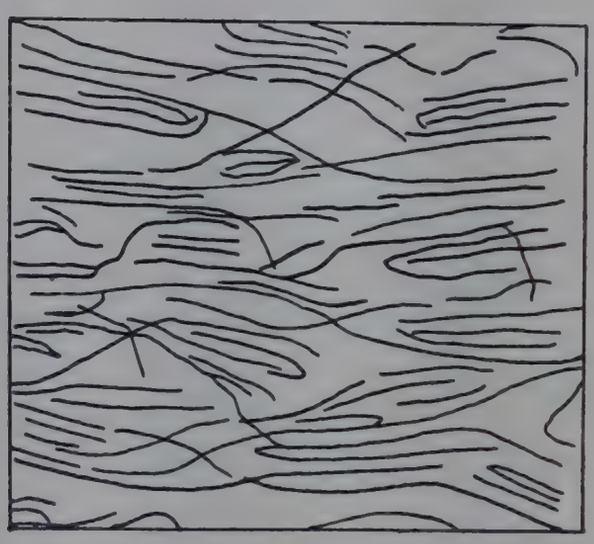
There are two ways in which the subject can be viewed. Cellulose may be considered as a linear polymer containing a number of hydroxyl groups which make a variety of typical chemical modifications possible. One might then list together all the type reactions under suitable categories, e.g., esterification, etherification, oxidation and xanthation, and consider the different useful properties resulting from such reactions. Alternatively, cellulose may be considered as a fibrous material exhibiting a number of useful or defective textile properties and then consider ways and means of chemical modification with a view to rectifying the defective properties. The objective of this paper is to focus attention on what has been done or can be done to improve the textile properties of cellulose by taking recourse to chemical modifications.

PROPERTIES OF TEXTILE CELLULOSE

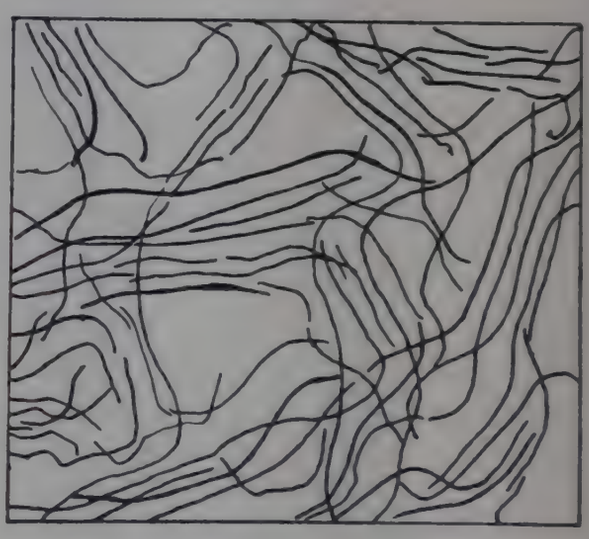
The following are a few of the numerous textile properties of cellulose : warmth; drape; resilience and drape; elasticity and strength; lustre;



Crystalline regions (C) and Amorphous regions



Random orientation



Parallel orientation

FIG. 2—ORIENTATION IN CELLULOSE MOLECULAR CHAINS (DIAGRAMMATIC)

crease-resistance; dimensional stability; spinnability; abrasion and flex resistance; heat, sound and electrical insulation; quick drying; water repellency; air permeability; resistance to mildew and rot-proofness; absorbency; wash resistance; and soil resistance.

The relative importance of one or more of these properties, however, varies from country to country, climate to climate and dress habits of different people. Moreover, it is ultimately the end use that determines the exact manner in which one or more properties are selected or modified. However, the properties can be broadly grouped[4] under the following headings :

Properties based on polymer structure — (i) elongation and elastic properties; (ii) flex resistance, tear strength and wear life; (iii) wet strength, dimensional stability and wash resistance; (iv) crease-resistance and drape; and (v) bulk density and warmth.

Properties based on form, dimensions and surface characteristics of fibre— (i) lustre; (ii) slipperiness and clinging resistance (iii) resistance to soiling; and (iv) permeability.

Properties based on hydrophilic or hydrophobic characteristics— (i) Water repellency; (ii) absorbency; (iii) quick drying; (iv) electrical insulation; (v) dye-receptivity; and (vi) moisture regain.

Properties based on structure— (i) mildew- and rot-resistance; (ii) resistance to deterioration by light, heat, chemicals, etc.; (iii) flame resistance; and (iv) ion-exchange properties.

Elongation and elastic properties

Almost any treatment which changes the molecular packing in cellulose will have a significant effect on these two properties. The simplest and the most striking example is treatment of cotton yarn under tension with steam, whereby the elongation is considerably reduced; such destretched yarns find commercial application in the manufacture of improved tyre cords. References to literature are too numerous to mention here, but a process developed at the Shri Ram Research Institute[5] three years ago is worth mentioning. The yarns were dipped in a mixture of amyl and butyl alcohol for a short time and then stretched and steamed to remove the solvent. Increase in tenacity of the order of 50—80 per cent was recorded. Unfortunately, the method could not be utilized commercially due to various considerations.

Another example of a simple chemical treatment which altered the elastic properties of cellulose comes from the Southern Regional Laboratory[6] in U.S.A. Bandage fabric was mercerized in caustic soda washed and dried without tension. Such bandage has more desirable properties and a much higher elongation (35%) than untreated material. It fits the various parts of the human body more efficiently due to its elastic nature[7-9].

A third and extremely important chemical method of altering the elongation and elastic properties of cellulose is by reaction involving the use of cross bonding agents.

Flex life, tear strength and wear life

It is being more and more realized that changes in the crystallinity of cellulose can be brought about by chemical means[10]. Segal *et al.*[11] treated native cotton with aliphatic amines and obtained cottons with varying degrees of crystallinity. It was thus possible to bring down the crystallinity from 90 to as low as 25 per cent. The treated cottons show altered dyeing properties, improved chemical reactivity[12], better flex life and improved tear strength[13]. Further evaluation of such decrystallized cotton had been handicapped by lack of enough treated material for test purposes. It appears, however, that Greathouse *et al.*[14]

have succeeded in trying the process on a pilot plant scale and increasing developments may be expected in the near future.

Wet strength, dimensional stability, wash and crease-resistance and drape

All these related properties have assumed importance since the introduction of regenerated cellulose fibres, and have been largely improved by cross bonding and by aminoplast resin modification. Considerable attention is being directed towards the treatment of cotton in this way, and the introduction of silicone resins and nitile lattices[15] along with the conventional urea-formaldehyde or melamine-formaldehyde resins, need special mention here, as they seem to overcome some of properties to a significant extent[4].

Though drape is associatd with yarn and fabric construction, it would appear that decrystallization and cross linking could improve these properties to a significant extent[4].

Bulk density and warmth

These properties do not appear to have received as much attention as they deserve. It would perhaps be safe to assume that these two properties are inter-related and that warmth can be increased by changes in bulk density. In an excellent review on the thermal properties of textiles, Morris lists a number of physical factors that contribute to the thermal characteristics of textiles, such as specific heat, bulk density and conductivity. However, there appears to be little work done on the chemical modification of cellulose from this point of view. An interesting development[16] for improving the heat retaining properties of textiles is the use of metallic flakes in the binding polymer sprayed on the surface, followed by baking. It is claimed that the fabric retains its permeability and at the same time, due to cloth shrinkage, the trapped air aids insulation. In a country like India, attempts to make cotton more warm may prove useful in the long run.

Lustre

So far, chemical methods to enhance lustre have been restricted to the use of mercerization. There have been numerous investigations on caustic mercerization and the latest series of papers by Fourt *et al.*[17-19] are worthy of mention.

The treatment of cotton with a strong solution of caustic soda changes the crystal structure of cotton cellulose from cellulose I to cellulose II (Fig. 3 and Table 1). The factors involved in the development of lustre have been summarized by Marsh[20].

There have been notable contributions in the resin treatment of textiles with a view to obtain permanent lustre[21, 22]. In all such processes, the materials are treated with resins, dried and schreinered or calendered, and then cured. The effects obtained are made wash resistant.

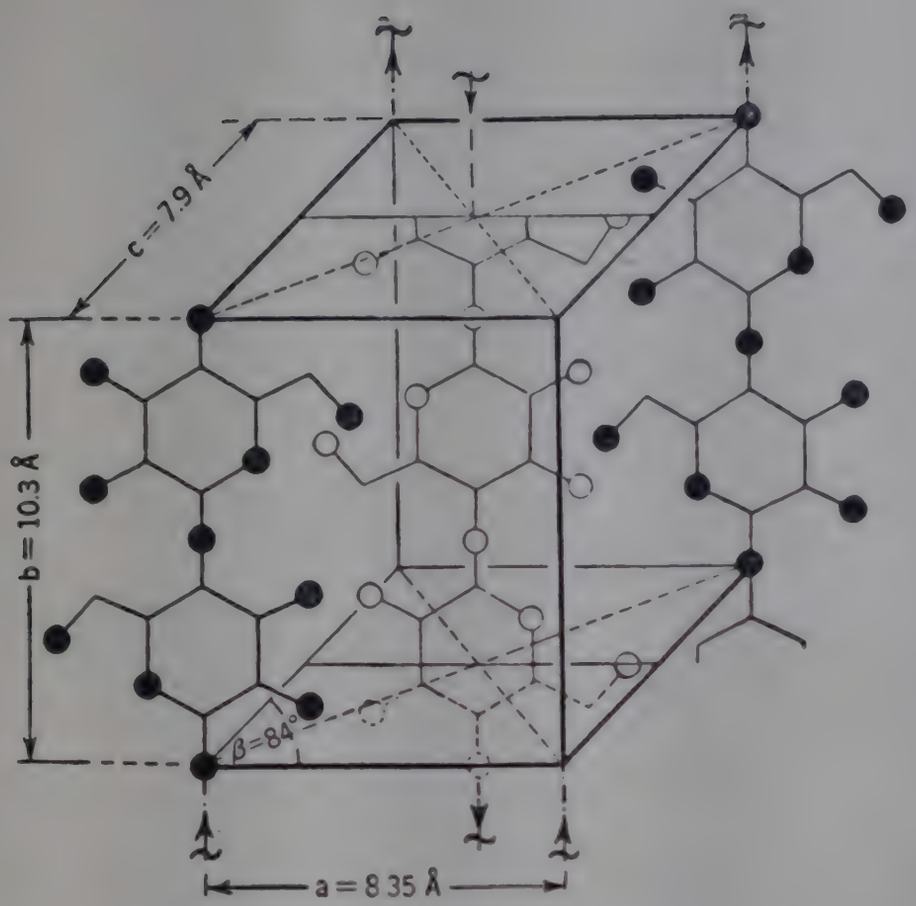


FIG. 3—UNIT CELL OF CELLULOSE I (*after* MEYER *et al.*)

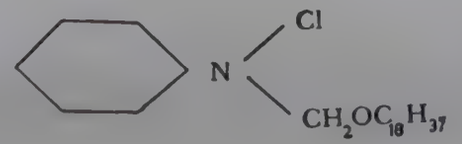
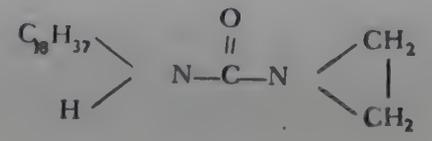
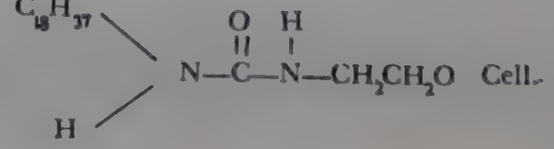
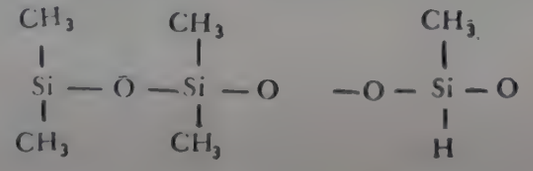
Slipperiness and resistance to clinging

There does not appear to be any significant work on the improvement of slipperiness and clinging resistance of textile yarns. Presumably these properties may be improved by treatment with reagents which influence surface smoothness of cotton cellulose or protruding lint. Attaching lubricating groups to the cellulose chain may be particularly useful. This aspect is important from the viewpoint of drafting and spinning, particularly in the spinning of blends of cotton with other fibres. It is rather surprising that these aspects have attracted so little attention.

TABLE 1—THE UNIT CELL STRUCTURES OF POLYMORPHIC FORMS OF CELLULOSE

AXIS	CELLULOSE I	CELLULOSE IV	CELLULOSE II	CELLULOSE III
a	8.35 A.	8.11 A.	8.1 A.	7.74 A.
b	10.3 A.	10.3 A.	10.3 A.	10.3 A.
c	7.9 A.	7.9 A.	9.1 A.	9.9 A.
β	84°	90°	62°	58°

TABLE 2—CHEMICALS USED FOR IMPARTING WATER REPELLENCY TO CELLULOSE FABRICS

Chemical	Formula	Type of reaction
Aluminium chloride + ammonium salts of weak organic acids		Deposition of insoluble salts on fibre
Zirconium salts of water-soluble fatty acids		Deposition of insoluble salts on fibre
Octa-decyloxymethylpyridinium chloride		Capable of entering into chemical combination with OH groups
Esterification with organic isocyanates, such as N-octa decyl-isocyanate	$C_{18}H_{37}NCO$	$C_{18}H_{37}NCO + Cell.OH$ $Cell.O.CONHC_{18}H_{37}$
Synthetic compounds of high molecular wt., hydroxymethyl urea, & N-Hydroxymethyl-amide & higher fatty acids		Probably lowers the imbibition value
Octadecylethyleneurea (Persistol vs.)		
Silicones: (i) Dimethyl siloxane polymer (ii) Methyl hydrogen siloxane polymer		Resin formation

Resistance to soiling

It has been shown by Compton and Hart and others[23-25] that cotton treated with carboxy methyl cellulose and certain other polymers possesses improved anti-soiling properties. Ultermohlen[25] studied the effect of various substances on resistance to soiling and ease of soil removal and concluded that all treatments which altered the electric charge on the surface of the fabric affected the soil retention properties of textiles. Effects of carboxymethylation, anion and cationic surfactants, partial acetylation, etc. have all been studied. This subject is still receiving attention and it may be predicted that future trends will be towards further efforts in this direction.

Permeability

Though considerable theoretical investigation has been carried out on permeability, very little work connected with the deposition of natural and synthetic rubber lattices has been reported.

Water repellency, absorbency, quick drying, electrical insulation and dye-receptivity

These properties are related to the existence of hydrophilic groups in textile fibres, e.g., $-NH_2$-OH, COOH, -CONH, etc. It is natural, therefore, that attempts at modifying these groups should have been made and are continuously being made. In the conventional method, insoluble aluminium or zirconium salts of fatty acids, with or without wax emulsion, are made to be adsorbed on the fibre surface so that adherence is achieved due to chelation of the polar group in the fibre with the metal ion, and water repellency is achieved due to the hydrophobic nature of fatty acid molecules. Improvements in this method continue to appear in patent literature[26-28]; but the materials treated by such processes show inferior resistance to washing and dry cleaning, and research at present is being concentrated on permanent water-repellent finishes.

A notable devlopment in this connection is the application of organo-silicon compounds[29, 32] to textiles. Net in importance may be mentioned the use of condensation resins with or without admixture with water-repellents. Mention may also be made of the application of high molecular weight organic isocyanates, particularly octadecyl-isocyanate[32]. This treatment appears to have been utilized, in Germany, on a commercial scale during the last war.

Absorbency may be described as the reverse of water-repellency, and there appears to be little need for chemical modification of cellulose fibre, because the hydroxyl groups are sufficiently hydrophilic. The main attempts in this direction relate to treatments with swelling agents like caustic soda which are known to change the molecular structure. Moisture and dye-receptivity are also closely related to this property. However, partial carboxymethylation[34, 35] appears to improve these properties in a

substantial manner and further work in this direction is being undertaken at the Shri Ram Institute.

Considerable literature on theoretical aspects[36] is available on the electrical properties of cellulose and it has been established that this property largely depends on the hydrophilic nature of hydroxyl groups in cellulose. Naturally, all treatments which affect moisture relations also affect the electrical properties of cellulose.

The literature on water repellency is too vast to be given here in any detail. Some typical agents which are used for chemical modification for increasing the hydrophobic nature of cellulose are listed in Table 2.

Mildew- and rot-resistance

These properties are important from the point of view of storage and for outdoor use. They have been achieved by etherification and esterification[37, 38]. For instance, durable rot-resistance is attained by etherifying with acetic anhydride. Another esterification reaction that has been commercially applied to cotton is phosphorylation. In this process, cotton fabrics are padded with an aqueous solution of phosphoric acid containing urea, then dried and cured[35] at 140°C. Cross bonding agents and aminoplast resins are also known to improve mildew- and rot-resistance. The use of copper organic, inorganic, organic sulphur, mercuric, phenolic and quaternary ammonium compounds have also been mentioned. The field is large and cannot be covered here adequately. The Technical Development Establishment Laboratories at Kanpur and the Indian Jute Mills Association Research Institute at Calcutta appear to have done commendable work in this field. Some typical reagents used for this purpose are listed in Table 3.

Heat and flame resistance

Both acetylation[39] and cyanoethylation[40] are known to improve the heat resistance of cotton. Reeves and Guthrie[41] have described the use of tetrakis-hydroxy methyl-phosphonium chloride (T.H.P.C.) for obtaining flame resistance. Frick *et al.*[42] have described treatment with an aqueous emulsion of an organic polymer prepared from bromoform and trialkyl-phosphates for obtaining effective and comparatively cheap flame resistance. Some of the reagents used in the treatment are listed in Table 4.

Ion-exchange properties

Several chemically modified fabrics of cotton have been prepared which exhibit ion-exchange properties similar to those of the well-known grandular ion exchangers[43]. They are produced by the interaction of substituent groups with basic or acidic properties with the cellulose molecule under such conditions that the fabric structure is retained. For example, phosphorylated cotton fabrics behave like a dibasic acid,

TABLE 3—CHEMICALS USED FOR IMPARTING MILDEW- & ROT-RESISTANCE TO CELLULOSE FABRICS

Inorganic chemicals:

(i) Copper salts (ii) Chromium salts (iii) Zinc salts

Copper organics:

(i) Copper naphthenate (ii) Copper quinolinolate

Phenolic compounds:

(i) Tri-, tetra-, penta-chloro phenols (ii) Tetra-bromo-ortho cresol (iii) 2-bromo-4-phenyl phenols (iv) *p*-Nitro phenol (v) Salicylanilide (vi) 2-2'dihydroxy 5:5' dichlorodiphenyl-methane

Mercuric compounds:

(i) Phenyl mercuric acetate, Phenyl mercuric oleate, Phenyl mercuric linoleate
(ii) Pyridyl mercuric chloride, Pyridyl mercuric acetate, Pyridyl mercuric stearate

Sulphur compounds:

(i) Derivatives of 2-mercapto benzothiozol (ii) Dithiocarbonic acid

Quaternary compounds:

(i) Trimethyl ammonium chloride (ii) Lauryl pyridinium bromide (iii) Chloro benzyl quaternary ammonium salts

Tetrakis (hydroxymethyl) phosphonium chloride (T.H.P.C.) $(HOCH_2)_4PCl$

Partial cyanoethylation of cellulosic materials

Urea, melamine, formaldehyde resins

TABLE 4—CHEMICALS USED FOR IMPARTING FLAME & HEAT RESISTANCE TO CELLULOSE FABRICS

Flame Resistance:

Antimony oxide and chlorinated wax or rubber and vinyl chloride resin; Combination of antimony and titanium oxide, e.g., "Erifon" (Dupont); Mixture of zinc oxide, zinc carbonate, boric acid, chlorinated wax and vinyl chloride resins; Melamine polyphosphate resins, e.g., Pyroset DO; Polymer of bromoform and alkyl-phosphate; Urea phosphate; Insoluble phosphorus condensation products of phosphorus oxychloride and ammonia, along with alkyl phenolic or amino resins; Phenolic resins and the complex addition product of melamine and P_2O_5; Bis-2-chloroethyl chlorophosphonate; Tetrakis (hydroxymethyl) phosphonium chloride (T.H.P.C.) $(HOCH_2)_4PCl$

Heat Resistance:

Guanidine salts of acids; 2-2'Diaminodialkylsulphide $S(C_2H_4NH_2)_2$; Organic amines, e.g., ethylene diamine n-butylamine; Partial acetylation of cellulosic material; Cyanoethylation of cellulosic material

with acid strength comparable to that of the first and second hydrogens of phosphoric acid. Partially sulphethoxylated cellulose is a strong acid cation exchanger, whereas carboxy methylated cellulose and the succinic acid half ester of cellulose are weakly acidic cation exchangers. Amine ethyl celluloses and diethyl amine ethyl celluloses are weakly basic anion exchangers.

Chemical modification of textile celluloses offers a wide field for research and development. Short staple Indian cottons, though possessing some

drawbacks from the spinners' point of view, are particularly attractive as raw material for chemical modification.

Chemical modification involves two important industries—the chemical manufacturing industry and the textile processing industry. Effective collaboration of the two industries is an important consideration for those concerned with research and development in this field.

Effective collaboration of the Chemical Research Committee and the Cellulose Research Committee seems to be desirable. As many of the newer chemicals mentioned in this review are not available in the country, the textile industry is at a disadvantage and is unable to try them.

In the context of the present day needs, the following lines of research and development would be fruitful: manufacture and use of silicone resins for textile applications; (ii) acrolein and its polymers for cellulose modification; (iii) acrylonitril and its polymers for textile application; (iv) decrystallization of cotton; (v) partial etherification; (vi) partial esterification; (vii) application of reactive manomers and condensates; and (viii) application of cross bonding compounds.

Acknowledgment

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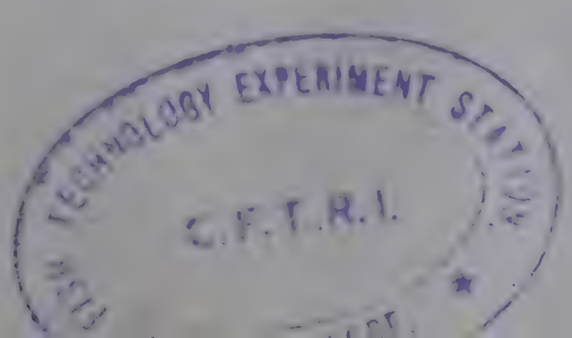
Discussion

Dr. H. Wakeham: The figures given by the author for the requirements of cotton for its different properties are very rough, and in certain cases, as for example, in crease recovery, the actual consumption is far more. Also, while the Southern Regional Laboratory, U.S.A., had been working for years on various chemical modifications of cotton, none if these processes was yet commercially used to any significant extent except that of acetylation.

Dr. V. B. Chipalkatti: I agree with the remark, but from the point of view of tailor-made cotton products for specific end uses, chemical modification offered many possibilities. With improving techniques in textile treatment, more and better methods of obtaining chemical modifications are to be expected. For instance, the fluid-bed technique for textile treatment on which I am now working may be applied to textile modifications, and thus a new field of development may be expected.

Shri L. R. Sud: Mention has been made of various improvements in the properties of cotton through chemical modification. However, the overall changes in the properties of such modified cellulose should be considered. For instance, our experience shows that partial acetylation of cotton fabrics, although increasing resistance to micro-organisms, adversely affects the resistance of cotton to actinic attack.

Dr. V. B. Chipalkatti: I agree.



Nitrocellulose

K. S. VARADACHAR

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The characteristics and uses of nitrocelluloses have been discussed. The displacement and mechanical methods of nitration and their relative merits have been set out and the manufacture of nitrocellulose in the Cordite Factory, Aruvankadu described. The scope for the development of the nitrocellulose industry has been briefly indicated.

Nitrocellulose, a misnomer for cellulose nitrate, is an important commercial product. It is an essential ingredient of blasting explosives, and a base for propellants. It is also used in the celluloid and lacquer industries.

Braconnot in 1832 observed the formation of inflammable materials by the action of nitric acid on cotton, starch and wood fibre, and obtained impure products which he called xyloidines. Pelouze in 1838 investigated the action of nitric acid on cotton. The technological importance of the process was recognized in 1846 by Shonbein who took out a patent for nitrated cellulose obtained by treating cotton with a mixture of nitric and sulphuric acids. The products obtained by him were, however, unstable and there were some serious explosions, the worst being the one in Faversham in 1847. This led the governments in several countries to ban its manufacture and use.

Subsequent progress was in the direction of preparing a stable product and the classical researches of Abel led to the understanding of the causes of instability, and to the manufacture of stable nitrocellulose.

The general reaction for the nitration of cellulose may be indicated by the following equation :

$$C_6H_{10}O_5 + xHNO_3 \longrightarrow C_6H(10-x)O_5\ (NO_2)_x + xH_2O$$

where x is not greater than 3.

The three alcoholic groups—two secondary and one primary—present in each glucose residue of the cellulose chain may react giving three or more compounds corresponding to the successive nitration of the three hydroxyls. The final product of the reaction should be trinitrate $C_6H_7O_5(NO_2)_3$ with a nitrogen content of 14.15 per cent, but it is not

possible to obtain a stable product with this nitrogen content by the action of sulphuric and nitric acid mixtures. By using special techniques, it is possible to obtain a product nearing this theoretical composition. However, in actual practice, a series of substances with nitrogen contents varying from 10–13.5 per cent are prepared. The various grades of nitrocellulose usually met with in industry, and their uses are given in Table 1.

Nitrocellulose was first prepared in India at the Cordite Factory, Aruvankadu, which is even today the only factory producing it. Till very recently, the only use of nitrocellulose was for defence purposes. During the last three years, the Factory has been supplying nitrocellulose of grade (iii) to manufacturers of artificial leather, book binding cloth and lacquers, and so far 170 tons of this material has been supplied. It has been estimated that the paint industry will require 500 tons of nitrocellulose per annum during the second Plan period. The gelignite industry, sponsored by the Government of India, in collaboration with Messrs *Imperial Chemical Industries*, also uses nitrocellulose. Proposals for the manufacture of raw photographic films in India are also under consideration. Thus the demand for nitrocellulose is continuously rising.

The raw materials in common use are cotton, in the form of spinners' waste or linters, and paper. Where cotton is plentiful, linters constituted the cheapest raw material, as they are otherwise wasted and their removal is essential both for oil recovery from cotton seed and for utilizing the oilcake as cattle feed.

Process of production

Hard spinners' waste, available from textile mills, is used as the raw material at Aruvankadu. This material is expensive, as it finds other uses and has also a good export market. In England, paper in the form of scrolls or sheets, cut into small pieces, are used for nitration.

TABLE 1—GRADES OF NITROCELLULOSE

Grade No.	Nitrogen content %	Solvents	Uses
(i)	10.7–11.2	Ethyl alcohol	Plastics
(ii)	11.2–11.7	Methyl alcohol; ether-alcohol; ethyl acetate; acetone	Photographic films, nitrate rayons and lacquers
(iii)	11.8–12.3	Ether-alcohol: ethyl, butyl, and amyl acetates, acetone	Lacquers, artificial leathers, gelatinous explosives
(iv)	12.4–13.0	Acetone	Explosives, e.g., smokeless powder

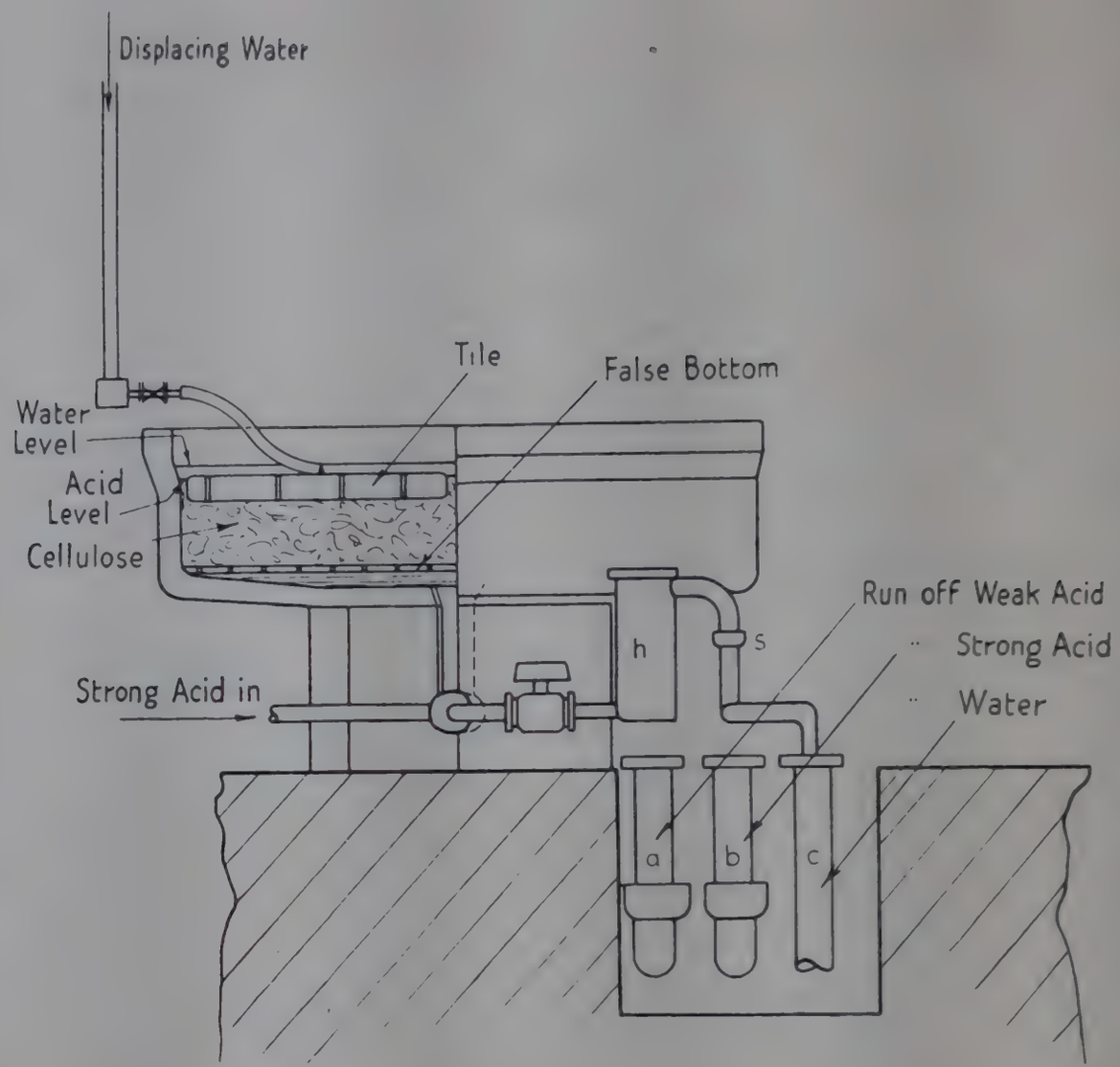

FIG. 1—PAN USED IN THE DISPLACEMENT PROCESS (DIAGRAMMATIC)
(*after* F. D. Miles, 'Cellulose Nitrate', 1955)

Cotton waste is first treated to remove waxes, lignin, hemicellulose, etc., by boiling with alkali under pressure, a process called 'kiering'. The kiered product is washed free of alkali and dried. The process of kiering, washing and drying has to be done under properly controlled conditions as otherwise the product tends to ball up or form knots and the penetration of acids in the subsequent treatment is hindered.

The displacement process (Fig. 1) is largely employed for the nitration of the cleaned material. The process consists in dipping the cotton in mixed acid for $2\frac{1}{2}$ hr. at the end of which the acid is slowly displaced by water.

The nitration unit consists of 4 pans, and each pan received a charge of $22\frac{1}{4}$ lb. of cotton and 6 cu. ft. of mixed acid. After $2\frac{1}{2}$ hr. during which the temperature ranges between 17° and 21°C., water is slowly let in at the top, while a corresponding quantity of spent acid is drawn off from the bottom. The spent acid is revivified by doping with nitric acid and used again. The hydrometer float shuts off the flow of acid as soon as the specific gravity falls to 1.250 and diverts it into waste. The following

are the working figures for guncotton manufacture : Acid composition—sulphuric acid, 70 ; nitric acid, 22 ; and water 8 per cent. Composition of recovered acid—sulphuric acid, 71.5; nitric acid, 18.5; and water 10 per cent. Yield, 170 per cent.

There are certain inherent disadvantages in this method. The mixed acid is troublesome to handle. On wet days it fumes heavily and in spite of efficient draught arrangements, handling is difficult. The feeding of dry cotton waste has to be carefully controlled. Only small quantities should be fed each time and rapidly pushed under the acid with stainless steel forks. Otherwise, local heating occurs with onset of decomposition. The maximum permissible moisture content of cotton is 2.5 per cent ; if this is exceeded pan fires are likely to occur. Sometimes, in spite of all precautions, fires set in with violent decomposition accompanied by intense fumes of nitrogen dioxide, which are dangerous. In view of the risks involved, the process does not find much favour. As against these disadvantages, the process is foolproof and requires comparatively little operational control. Small variations in composition of mixed acid, fairly wide variations in temperature and even time of nitration and displacement are accommodated. The quality of the batches is remarkably uniform.

The second method, which has found favour in many countries, is the mechanical process (Fig. 2). It consists of a constant volume reservoir, from which the mixed acid is measured out into the nitrator. Cellulose is added to the acid under stirring. The nitration is carried out for 20–45 min. at the end of which, the contents are emptied into a centrifuge and the acid separated. The wet nitrocellulose is rapidly drowned in a large volume of water and washed. The advantages of this method are : space required for the plant is small compared to the displacement process ; manual labour is reduced ; the process is clean and capable of practically continuous operation by having several units running in cycles ; the period of nitration is shorter ; and a wide range of cellulosic material can be used as raw material. Further, air-dried cellulose can be used. By altering the temperature of nitration by means of calorifiers, any type of nitrocellulose can be produced for commercial purposes. As against these advantages, the acid composition is to be rigidly maintained, and each manufacturer has to work out the conditions of nitration best suited for the raw material employed and the final product derived. Fires in the centrifuge are common ; it has been found that if the nitrated material is overcentrifuged and has less than a minimum acid content, the material tends to catch fire. Corrosion is a serious problem and maintenance costs are high. The chief drawback is that the nitrocellulose obtained is more unstable than that produced by the displacement process and requires more elaborate after-treatment. Further, the proportion of acid to cellulose is high (sometimes as high as 1 : 60, as against 1 : 30 in the displacement process) and the recovery of spent acid is poor.

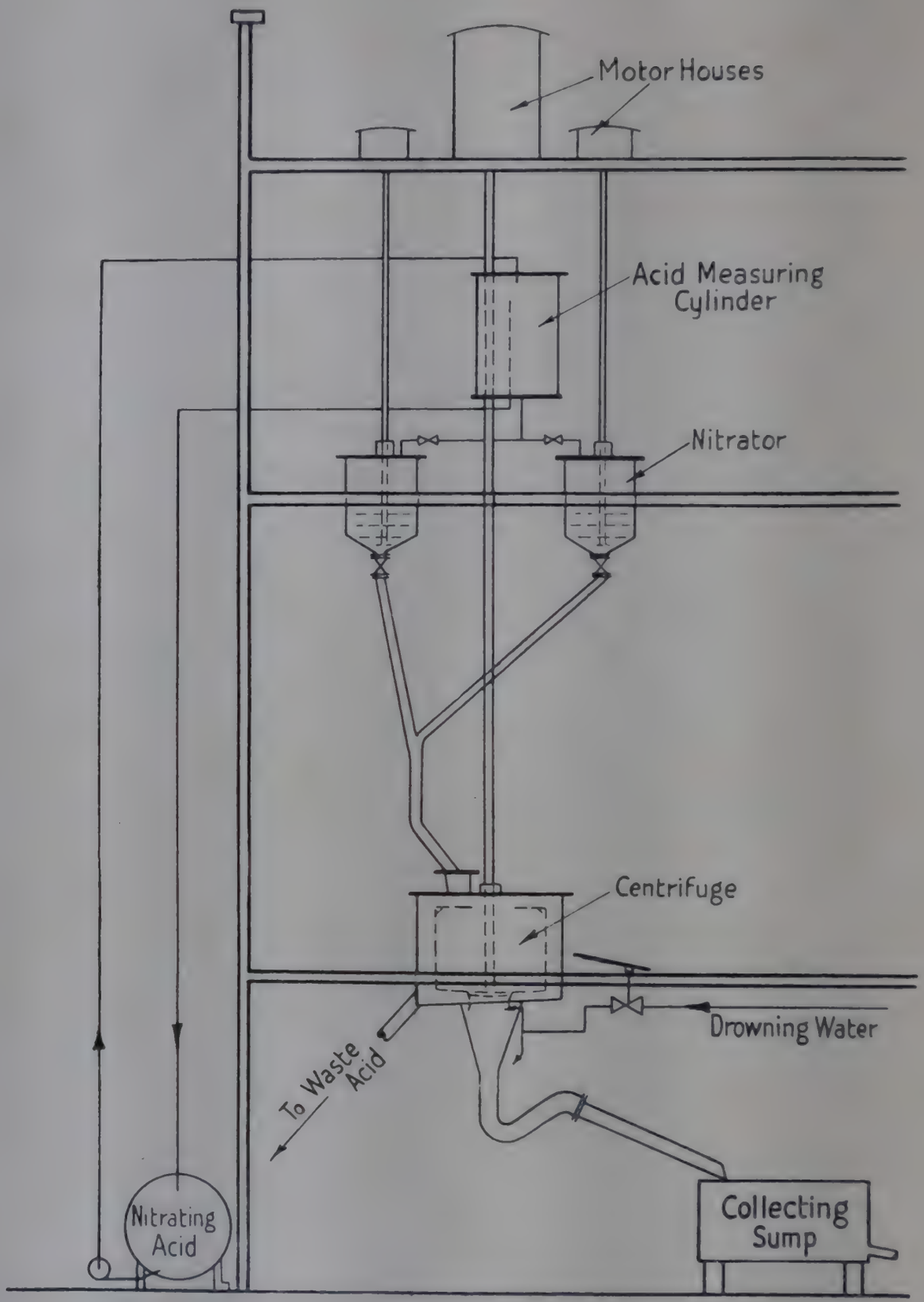

FIG. 2—MECHANICAL PROCESS (DIAGRAMMATIC) FOR THE NITRATION OF CELLULOSE (*after* F. D. Miles, 'Cellulose Nitrate', 1955)

The nitrated fibre is boiled in lead-lined vats a number of times, with changes of water between boils. The initial acidity which is *c.* 0.10 per cent goes down to 0.04 per cent. In Aruvankadu (height above sea level, 6,000 ft.) normally two boils of 8 hr. duration at a pressure of 7 lb./sq. in., corresponding to a temperature of 105°C. are done.

The stabilized material is beatered in hollanders, of the type used in paper industry, in a faintly alkaline medium. It is subjected to a series of washes, called potchering, to remove impurities. Finally, as nitrocellulose is liable to slow decomposition even at ordinary temperatures of storage, a small quantity of finely divided precipitated chalk is added to the material to neutralize any acid that may be produced during storage. The material is then centrifuged and sold either 'alcohol-wet' or 'water-wet'. For some special uses, diphenylamine (1%) is used as stabilizer.

Nitrated cellulose retains most of the physical characteristics of the original raw material, except that the fibres are hard and brittle.

Effect of varying nitration conditions

Despite the wide range of permissible variations in the proportions of nitric acid, sulphuric acid and water in industrial practice, the selection is limited by considerations of cost and also of the marked swelling or dissolving action on the fibre exhibited by some of the compositions. Using cotton waste as raw material and the displacement process for nitration, a mixed acid containing sulphuric and nitric acids in the ratio of 1 : 3, gives a nitrocellulose containing 13 per cent nitrogen ; with a mixed acid containing : sulphuric acid, 62.5 ; nitric acid, 22.5 ; and water 15 per cent, a product containing 12.2 per cent nitrogen is obtained. Further, while the production with the first mixture is soluble in ether-alcohol (2 : 1) to the extent of only 10 per cent, the latter is completely soluble in the mixed solvent. This difference in solubility is one of the criteria for distinguishing guncotton from other types of nitrocellulose.

Nitration conditions have a significant bearing on the viscosity of the resultant product, a property of extreme significance in its use for particular purposes. It has been shown that by substituting anhydrous phosphoric acid or by using phosphorus pentoxide and nitric acid at 0°C., a very high degree of nitration is obtained, without significant degradation of cellulose. This method has been employed for estimating the degree of polymerization and molecular size of the original cellulose.

The main characteristics of nitrocellulose are its nitrogen content and viscosity. The latter depends on the raw material employed and the condition of nitration. The viscosity can be brought down to any limit, either by degrading the raw material before nitration or by depolymerizing the nitrated material by boiling under pressure. The latter is the preferred method, as the preliminary degradation of raw cellulose results in a friable material difficult to handle and entails heavy losses in processing. During pressure boiling, a certain amount of acidity develops

by hydrolysis and some nitrogen is lost. By suitable control of pressure and time, any required type of product can be produced. In some cases, as in the case of low-viscosity industrial nitrocellulose, pressure boiling achieves both stability and degradation.

In trade practice, ether-alcohol solubility provides the criterion for the grade of nitrocellulose. This solvent is scarcely suitable for viscosity determination. Acetone can also be used, but it is hygroscopic. The *Imperial Chemical Industries* use a mixture of 95 per cent acetone and 5 per cent water as solvent. Butyl acetate and ethyl acetate have also been used, but here again the purity of the solvent is important in viscosity determinations. In American practice, the solvent in use (Hercules solvent) consists of a mixture of 20 parts ethyl acetate, 25 parts alcohol and 55 parts toluol by weight, and viscosity determinations are made with a 1 per cent solution for highly viscous types and a 12.2 per cent solution for degraded material.

The molecular weight of nitrocellulose is determined by osmometric method. However, true values obtained by the method are different from those obtained by viscosity methods.

Properties and uses

Nitrocellulose is a highly inflammable hygroscopic material. In the dry state it rapidly absorbs moisture from air. In the loose form, it burns with extreme rapidity and in confined spaces leads to detonation. In the compressed form, it is a powerful explosive. When wetted with water, however, it is quite harmless; when the moisture content is 13 per cent, it is so safe that a compressed block of it can be drilled. The wet material is still a powerful explosive, but the explosive has to be initiated with a powerful start. Usually, a dry primer is used for this purpose. Table 2 gives some of the explosive properties of wet and dry guncotton.

A remarkable feature of nitrocellulose is that when gelatinized by the use of acetone or a mixture of ether and alcohol, the product obtained, which has a horn-like appearance, burns slowly. This property is made use of in producing smokeless powder, particularly for sporting purposes. Even today, the main propellant for American artillery is nitrocellulose gelatinized with ether-alcohol and extruded into small grains 0.1–0.3 in. diam.×0.1–0.75 in. long.

When nitrocellulose is treated with nitroglycerine (another powerful explosive) it is converted into a tough horny mass, which burns slowly layer by layer. The rate of burning can be controlled by adding diluents like petroleum jelly and dinitrotoluene. By regulating the shape and diameter of the strand, the rate of burning can be controlled to any desired extent. This process forms the basis of all propellants used in

modern artillery. The material is extruded and made available in the form of strands, called cordite.

Alexander Parkes showed that castor oil and camphor are excellent plasticizers for nitrocellulose. 'Celluloid', a product obtained from nitrocellulose, is soluble nitrocellulose (containing *c.* 11.2% nitrogen with low viscosity) plasticized with *c.* 25 per cent camphor. In practice, wet nitrocellulose is dehydrated in hydraulic presses and alcohol pumped in to replace the water. The alcohol-wet material is mixed with a solution of 50 per cent camphor in alcohol, the plastic mass filtered through cotton fabric under hydraulic pressure to remove impurities, and rolled on hot rolls at 50°C. when most of the alcohol is removed. It is then heated to nearly 100°C. at a pressure of 350 lb./sq. in. for 4–5 hr., conditioned at an even temperature for 24 hr. and then sheeted, dried and polished.

For photographic and cinema film purposes, resistance to moisture is important. A nitrocellulose with higher nitrogen content (*c.* 12%) is used and the camphor content limited to 10–15 per cent. The mixture is made into a viscous solution in ether-alcohol, freed from air bubbles and run in a thin layer on large revolving drums or moving bands which are covered with a layer of hard gelatine to give a smooth surface. The solvent rapidly evaporates in the enclosed space surrounding the wheel or band, and the hardened film is stripped off continuously under tension and dried. The final product contained about 3 per cent solvent.

Another industry that uses nitrocellulose in large quantities is the lacquer industry. Nitrocellulose containing *c.* 11.5 per cent nitrogen is mixed with various resins and plasticizers, pigments, colouring matter, etc., to give products which on application and drying give hard weather- and wear-resistant glossy surfaces.

TABLE 2—EXPLOSIVE PROPERTIES OF WET AND DRY GUNCOTTON

Material	Insensitiveness*	Rate of detonation *m./sec.*	Ignition point °C.	Total gases *cc./g.*	Heat of decomposition *cal./g.*
Dry guncotton	23	7300 (1.15)†	187	850 (1.15)†	960 (1.15)†
Wet guncotton (13% water)	70–100	5500 (1.23)†	187	900 (1.2)†	750 (1.2)†

* Value for picric acid, 100

† Figures within brackets represent densities at which values were obtained

Further Research Necessary

So far, nitrocellulose has not been the subject of any extensive study in India, perhaps because its production is confined to the Ordnance Factory. With the present tempo of industrialization, and the scope for starting industries which use nitrocellulose as basic material, there is need for extensive research on this important cellulose derivative. The possible lines for investigation are : survey of raw materials suitable for the production of nitrocellulose, conditions of nitration that will yield various types of nitrocelluloses required by consuming industries.

The Forest Research Institute, Dehra Dun has undertaken studies on the utilization of indigenous woods as sources of cellulose for paper production. We have obtained samples of wood celluloses and carried out laboratory investigation. Bamboo pulp holds promise, but further work and pilot plant trials are necessary for obtaining definite conclusions. There is need for intensive and extensive investigations on cellulosic material. It is hoped that other research institutions would take up work in this field.

Acknowledgment

My thanks are due to the Superintendent of Development (Military Explosives), Kirkee for his keen interest in the work, and to the Director of Research and Development (Armaments), Ministry of Defence, New Delhi for permission to contribute the paper.

Discussion

Shri T. S. A. Padmanabhan: The solubility of nitrocellulose in acetone is influenced more by uniformity of nitration than by the actual degree of nitration. For example, we have prepared a sample of nitrocellulose using 90 per cent fuming nitric acid alone, which had a nitrogen content of 13.2 per cent but was insoluble in acetone. On the other hand, a sample nitrated by a mixture of phosphoric acid and nitric acid gave a nitrogen content of 12.5 per cent but was completely soluble in acetone. In the latter case, one would expect more even nitration due to the swelling of the fibres by phosphoric acid.

Dr. P. K. Choudhury: The average values for nitrogen content have very little significance and the uniformity of nitration in the different glucose residues should be considered. Considerable literature is available on the properties of nitrocelluloses with different nitrogen content.

Dr. T S. Subramanian: A certain amount of work particularly related to storage stability is necessary for our own conditions of raw materials, method of nitration, etc. Such information is not easily available from other countries because of security reasons.

Anatomical Studies on Indigenous Hardwoods with Special Reference to their Suitability for Pulp and Paper

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Criteria based on anatomical studies, which may be applied for screening of hardwoods and selection of suitable ones for pulp and paper have been discussed. A list of hardwoods suitable for pulp and paper manufacture, together with their characteristics has been appended.

Cellulosic raw materials on which the pulp and paper industry depends, are essentially of plant origin, and apart from rags and old paper stock, they are derived from three main sources, namely, grasses including bamboo and bagasse, conifers or softwoods, such as spruce (*Picea* spp.) and fir (*Abies* spp.), and broad-leaved species, such as yellow poplar (*Liriodendron tulipifera* Linn.) and cottonwood (*Populus* spp.). Softwoods constitute the main source of supply in Europe and America, while in India, the chief raw material in use at present is bamboo. This is due to the fact that softwoods like spruce and fir which are best suited for pulping are found in India only at high elevations and in inaccessible regions, which makes their extraction difficult and expensive. On the other hand, supplies of bamboo are not adequate to meet the growing needs of the pulp and paper industry. Therefore, if the country is to aim at self-sufficiency regarding its paper requirements, the only alternative is to exploit the third chief source of raw material, namely, hardwoods.

The raw material, whatever be its source, is subjected to certain treatments, mechanical, chemical or a combination of both for converting it into pulp. Controlled variations and modifications in the different stages of these processes may to some extent determine the ultimate quality and paper-making property of pulp[1]. But whatever be the method of treatment adopted, these processes are always subtractive and it is not possible to produce paper possessing properties which do not have some relation or other with the inherent structure and characteristics of the raw material[2]. Therefore, if the indigenous raw materials are to be utilized to the fullest extent for pulp and paper production, it is neces-

sary to have a proper understanding of their anatomical structure and properties.

The raw material for pulp and paper is made up of minute cells, each with a distinct wall of its own. These cells are of different types—fibres, tracheids, vessels, parenchyma, etc., which are found in varying proportions and differ in their shape, size and cell wall thickness (Figs. 6 and 10). The main cause of heterogeneity and consequent difference in pulping quality of different cellulosic raw materials is ultimately traceable to a large extent to variations in the proportions of different types of cells and their relative size and cell wall thickness. Apart from anatomical structure, other properties like density, colour, presence of extractives, etc. of the raw material also affect pulping quality to some extent.

Based mainly on a study of the anatomical structure of bamboo it has been possible to develop a process at the Forest Research Institute, Dehra Dun, by which the yield could almost be doubled[3].

Considerable work has been done particularly in U.S.A., on the relation between fibre characteristics of softwoods and their pulping quality[4, 5]. Bray, Paul, Pillow, and Chidester[6-9] studied the effect of growth variables, proportion of summerwood, compression wood, and variations in cell wall structure in pines, on the yield and quality of pulp. On tropical hardwoods, however, very little information is available, though considerable data have been published on the proportions of various kinds of tissues, as well as on fibre dimensions[10, 11]. Based on our experience of bamboos and conifers, an attempt has been made in this paper to describe and discuss briefly those characteristics of hardwoods which are likely to have a bearing on the yield and quality of pulp.

Criteria for Selection of Hardwoods

The number of hardwoods occurring in India is estimated to be *c.* 1,500. The hardwoods show a wider range of variation in their structure and properties than softwoods. In density, they range from extremely light (sp. gr. less than 0.20) to extremely heavy (sp. gr. more than 1.20), while in colour, they vary from white to jet black through various shades of grey, yellow, brown, red or purple; they show also a much larger variation in total extractives—from 4.3 to 38 per cent[12]. In addition, hardwoods show striking differences in structure, due to differences in the proportion as well as the distribution of different kinds of tissues and cell dimensions. Some idea of the wide variation in tissue volumes of hardwoods may be had from Table 1 (Kollmann).

Hardwoods thus offer a wide choice of material and the need is, therefore, all the greater to draw up criteria by which their suitability for pulp and paper could be assessed. Some of the more important properties are discussed below.

TABLE 1—PROPORTION OF DIFFERENT TISSUES IN HARDWOODS

Tissue (or cell types)	Proportion in volume, %		
	Min.	Av.	Max.
Libriform fibres	26	49	78
Vessels	5	20	58
Parenchyma cells	3	13	21
Ray cells	6	18	28

Specific gravity—Other factors remaining the same, the specific gravity of a wood may be expected to give some indication of its pulping quality. Variations in density affect not only the yield, but also the quality of pulp and the cost of production. Specific gravity of dry wood substance or cell wall matter (made up chiefly of cellulose, hemicellulose and lignin) is *c.* 1.5, while the average specific gravity of dry wood blocks is *c.* 0.5, thus indicating that about two-thirds of an average medium weight wood specimen is composed of air cavities. In other words, the specific gravity of a wood may be said to be an index or ratio of cell cavities to cell wall, i.e., its porosity or capillarity, on which, to some extent, depends the penetration of cooking liquors. Further, provided the proportions of the various tissues are approximately the same, the specific gravity is closely related to the cell wall thickness, which as will be seen later, has a bearing on the strength values of pulp and paper. High specific gravity may also indicate a high extractive content, which again is not a desirable characteristic. Thus from all these considerations, light to medium weight or moderately heavy timbers in the specific gravity range 0.35–0.65 are likely to be suitable for pulping. This is confirmed from actual experience, as most common pulpwoods in U.S.A. including hardwoods, such as aspen (*Populus tremuloides* Michx., sp. gr. 0.40), cottonwood *Populus deltoides* Barbi. and others, sp. gr. 0.37–4.43), yellow poplar *Liriodendron tulipifera*, sp. gr. 0.43), alder (*Alnus* spp., sp. gr. 0.43) and gum (*Liquidambar styraciflua* Linn., sp. gr. 0.53) belong to this class.

Colour—Like specific gravity, colour in wood is extremely variable. But within certain limits, it is usually more or less constant for a species. Hence, it is one of the factors to be considered in choosing the raw material for pupling, for it not only affects the colour of the final product, but also the cost of bleaching. In view of this, light coloured woods (white to light shades of grey, yellow, pink or brown) are perferred to those having darker colours. A survey of the more common pulpwoods in use in Europe and America supports this.

Heartwood—Many woods, when viewed in logs from their freshly cut end surfaces, show a whitish or lighter coloured outer zone of varying thickness (sapwood) and a very much darker coloured central core, commonly

known as heartwood. The heartwood is non-functional in the tree and its darker colour is usually due to abundant coloured deposits found in the cells and other extractives. Dark coloured heartwood is a disadvantage as in some cases it may constitute as much as 90 per cent of a log. However, dark heartwood is not a feature of all woods. There are quite a number of woods in which the distinction between sapwood and heartwood is not marked, the centre of the log being more or less of the same light colour as the outer portion or showing only a slight and gradually deepening tint. Among conifers, spruce and fir belong to this class, while among hardwoods used for pulping, aspen, cottonwood and alder are good examples. Himalayan fir (*Abies pindrow* Spach) and spruce (*Picea smithiana* Boiss), mango (*Mangifera indica* Linn.), banyan (*Ficus* spp.) and semul (*Bombax* spp.) are some of the common Indian woods which belong to this category. Provided they are suitable otherwise, timbers without any distinct dark coloured heartwood, or with only a small amount of heartwood are better suited for pulping than woods with large dark coloured heartwood.

Extractives—As stated earlier, the amount of extractives and deposits found in hardwoods shows considerable variation which may be somewhat related to specific gravity. Relatively high extractive content is invariably associated with dense and dark coloured woods, though this may not always be the case. Aspen (sp. gr. 0.40), which is light coloured and a favourite pulpwood, contains just over 4 per cent by weight of extractives. On the other hand, red cutch (*Acacia chundra* Willd.), one of the densest and heaviest hardwoods of India, is dark reddish brown in colour and contains 25–30 per cent of extractives. Microscopic examination (Figs. 1 and 2) shows that practically all the cells, including vessels and fibres, are filled with a dark coloured gummy substance which would retard the penetration of cooking liquors. A good pulpwood should therefore have a low content of extractives.

Resin or gum canals—Resin canals are extensive inter-cellular spaces or cavities lined all through by a special type of parenchyma cells, known as resin epithelium, which secrete or excrete resiniferous products of plant metabolism into the cavity. Such special resin-bearing structures may be vertically aligned or they may run horizontally through the ray tissue, and are found in both softwoods and hardwoods. All woods, however, are not characterized by the presence of this anatomical feature. Among Indian softwoods, Himalayan fir is normally devoid of them, while they form a striking feature of all pines (*Pinus* spp.). Among hardwoods, resin canals are usually characteristic of certain families like *Dipterocarpaceae* (e.g., sal and gurjun), *Anacardiaceae* (e.g., jhingan) and *Burseraceae* (e.g., salai, garuga). High resin content is bound to affect the yield and quality of pulp to a certain extent. Therefore, other factors remaining the same, woods without resin canals are likely to be

better suited for pulp and paper than those in which they constitute a regular anatomical feature.

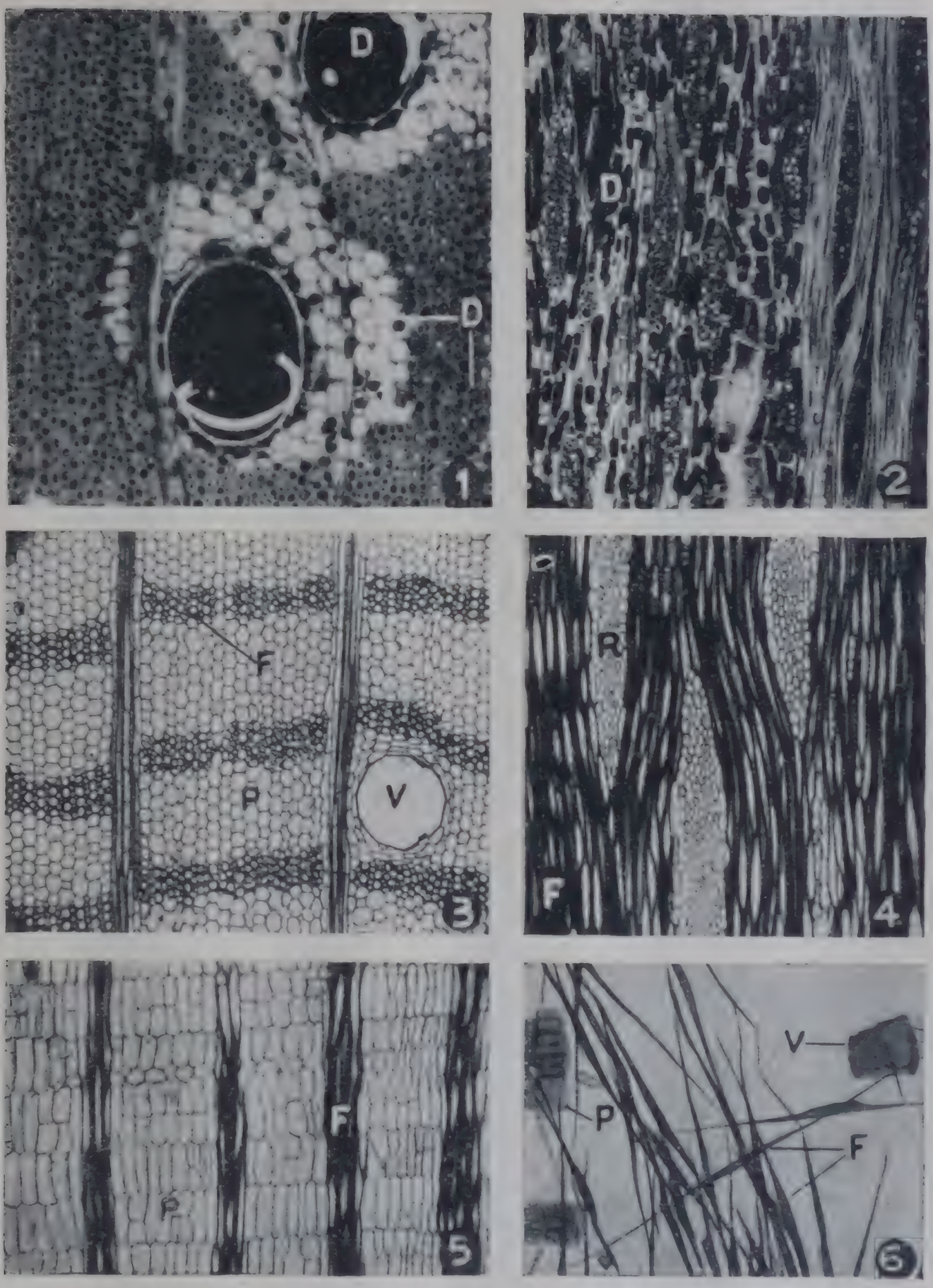
Amount and distribution of fibres—Microscopic examination of various wood pulps shows that tracheids in conifers and fibres in hardwoods form the principal constituents of the pulps, and are mainly responsible for yield as well as strength. The proportion of tracheids in softwoods and fibres in hardwoods, therefore, is an important factor in assessing their suitability for pulping. The figures given by Kollmann show that while the proportion of tracheids in conifers is relatively constant (87 to 95%, av. 91%), the fibre content of hardwoods is variable (26 to 78%). Only such hardwoods as contain a relatively high fibre volume are likely to be suited for pulping. The relative proportions of fibre tissue and their distribution in hardwoods could best be estimated from their anatomical structure as seen in microscopic sections cut in various planes (Figs. 3–5 and 7–9).

Size, shape and cell wall thickness of fibres—While the proportion of fibres mainly affects the yield of pulp, the size and cell wall thickness of fibres determine the quality of pulp and the strength of paper. Work carried out, particularly in U.S.A., leads to the conclusion that better pulp quality and higher strength value are usually associated with a marked increase in fibre (tracheid) length, though minor fluctuations occurring in hardwoods appear to be of no significance. Haywood has summarized the available data in these words: "the average strength value of all coniferous pulp is 113.3 with an average fibre (tracheid) length of 2.16 mm." while "the average strength of all deciduous pulp is 82.5 with an average fibre length of 1.02 mm." Thus, the greater strength of coniferous pulp appears to be related to fibre (tracheid) length, but is not directly proportional to it. In this connection, however, it must be borne in mind that the greater strength of softwood pulp may partly be due to the greater proportion of tracheids. Besides length, thickness of cell wall is also an important contributing factor for pulp quality. Experiments carried out at the U.S. Forest Products Laboratory on pine pulps containing various proportions of springwood (thin-walled) and summerwood (thick-walled) show that burst, tensile and fold values improve with an increase in thin-walled springwood tracheids. The tear values, however, tend to go up with an increase in the proportion of thick-walled summerwood tracheids. On hardwoods, some preliminary work has been done by Haywood who has estimated the fibre wall thickness of a number of selected North American hardwoods by actually measuring the wall thickness of the fibres. In the hardwoods examined by him, the area per cent of fibre cell wall was found to range from 22.8 in butternut (*Juglans cinerea* Linn.) to 82.7 in elm (*Ulmus americana* Linn.). On the basis of the behaviour of softwoods, such variations in fibre wall thickness may be expected to affect strength values. An increase in the proportion of thin-walled fibres is likely to increase the bursting, tensile

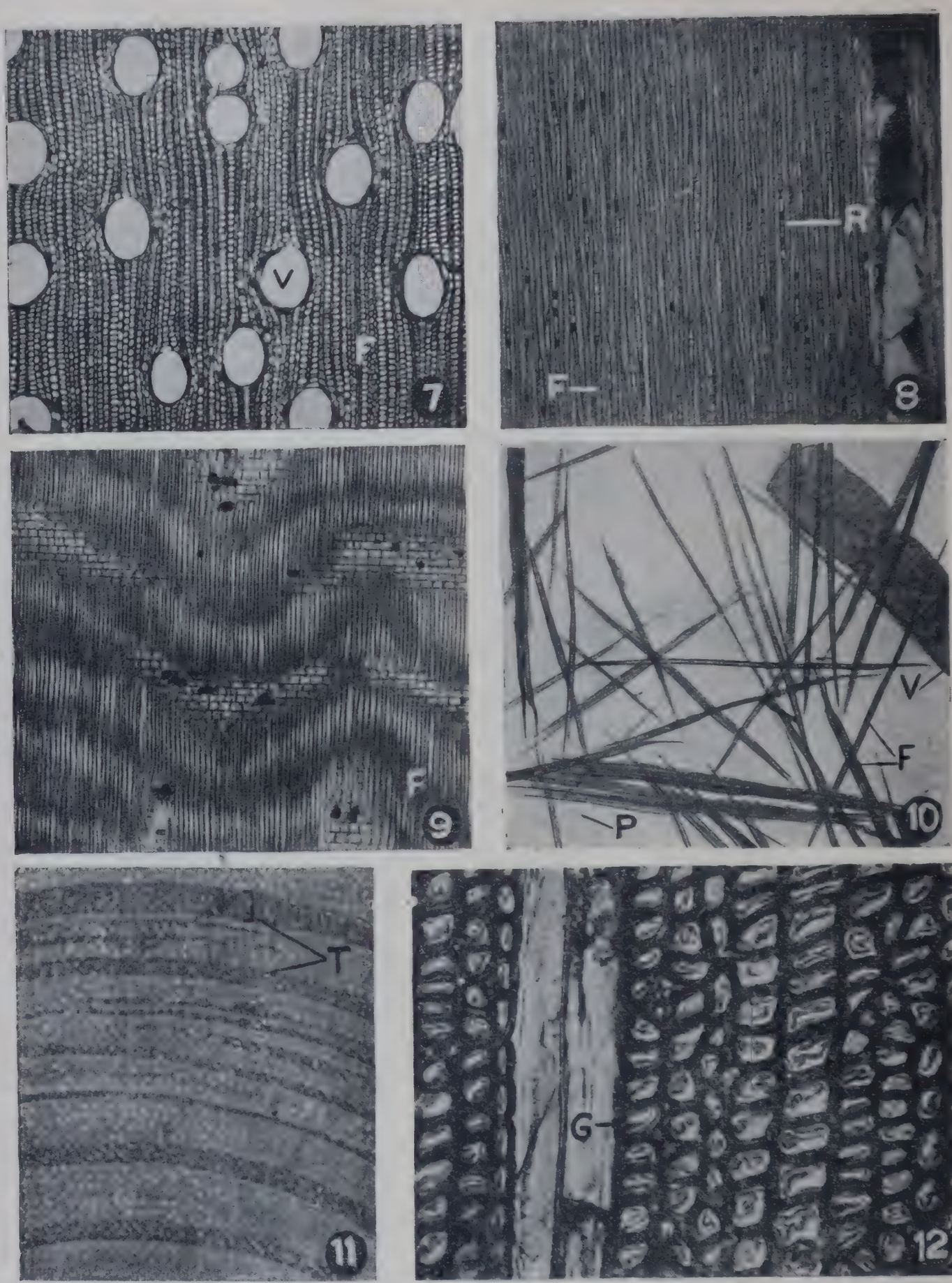
and folding strengths, while a preponderance of thick-walled fibres would tend to increase the bulk, opacity and tearing strengths. Indian hardwoods show marked difference in their fibre wall thickness due to wide variations in density. As fibre wall thickness could easily be measured in microscopic sections, it would be possible to use this criterion for assessing pulping quality. As regards shape, at the present state of our knowledge, it is not possible to say what possible effect variations in shape may have on the resulting pulp.

Minute structure of cell wall—Not only the thickness of fibre wall, but also the minute structure of the cell wall may have considerable effect on the strength properties of pulp. Not much work on this subject has so far been carried out on hardwoods, but the important bearing of cell wall structure is indicated by the data available for coniferous woods. Of the minute structural features of cell wall, which can be studied under the microscope, fibril angles in the secondary wall has received the greatest attention. Pillow *et al.* found that in loblolly pine (*Pinus taeda* Linn), pulps made from wood having fibrils oriented at large angles (30–45°) to the long axis of the tracheid were inferior in important strength properties to pulps made from wood with fibrils oriented at small angles (5–10°) to the major axis. Minute structural variations in the fibre walls of hardwoods may also have similar relation to strength and therefore require study. Other factors like variations in the relative thickness of middle lamella, primary wall and secondary wall may also afford scope for investigation.

Amount and distribution of parenchyma—Parenchyma cells are short, relatively thin-walled, brick-shaped cells with simple pits, found in all woods in varying amounts, in association with other tissues, like tracheids, fibres and vessels. Parenchyma cells may be aligned in a tree with their long axis vertical or horizontal. In the former case, they are termed longitudinal parenchyma or more often merely 'parenchyma'. In the latter case, they are arranged to form long, radial strips of tissue running from the pith towards the periphery and are called rays. Though strikingly differing in their arrangement and distribution, longitudinal parenchyma and ray parenchyma are essentially similar in structure and properties, and have the same effect on yield and quality of pulp. They are, therefore, considered here together under 'parenchyma'. Though both types of parenchyma cells together constitute a negligible proportion (3–10%) by volume of softwoods, in hardwoods, longitudinal parenchyma varies from 3–21 per cent (mean 13%) and ray parenchyma, from 6–28 per cent (mean 18%). Analyses of different softwood and hardwood pulps, as given by Haywood, confirm this statement. The proportion of ray and longitudinal parenchyma in coniferous wood pulps ranges from 3.7 per cent in douglas fir [*Pseudotsuga taxifolia* (Poir.) Britt.] to 8.7 per cent in hemlock [*Tsuga heterophylla* (Raf.) Sarg.], while in hardwood pulps, the total ray and parenchyma fraction varies from 6.8 per cent in



FIGS. 1–6. *Acacia chundra* Willd. 1—CROSS-SECTION (× 110); 2—TANGENTIAL SECTION (× 30) SHOWING ABUNDANT DARK DEPOSITS IN ALL CELLS. *Erythrina suberosa* Roxb. 3—CROSS-SECTION (× 30) SHOWING HIGH PROPORTION OF PARENCHYMA IN BROAD BANDS: 4—TANGENTIAL SECTION (× 30) SHOWING LARGE RAYS; 5—RADIAL SECTION (× 30) SHOWING LOW PROPORTION OF FIBRES; 6—MACERATED MATERIAL (× 30) SHOWING VARIOUS CELL TYPES (D, DARK DEPOSITS; F, FIBRES; P, PARENCHYMA; R, RAYS; V, VESSELS)



FIGS. 7–12. *Duabanga sonneratioides* Ham. 7—CROSS-SECTION (× 30) SHOWING HIGH PROPORTION OF FIBRES; 8—TANGENTIAL SECTION (× 30) SHOWING FINE RAYS; 9—RADIAL SECTION (× 30) SHOWING SCANTY VERTICAL PARENCHYMA; 10—MACERATED MATERIAL (× 30) SHOWING VARIOUS CELL TYPES. *Mangifera indica* Linn. 11—END SURFACE (NAT. SIZE) SHOWING PRONOUNCED TENSION WOOD (T); 12—CROSS-SECTION OF TENSION WOOD FIBRES (× 400) SHOWING GELATINOUS (G) SECONDARY WALL (F, FIBRES; P, PARENCHYMA; R, RAYS; V, VESSELS)

birch (*Betula* spp.) to over 28 per cent in oak (*Quercus* spp.). Indian hardwoods show a similar, or even more striking, difference in the amount of parenchymatous tissue (Figs. 3–5 and 7–9). This variation is of practical importance in the selection of raw material for pulping, as high parenchyma content lowers not only the yield, but also the quality of pulp. Parenchyma cells contain more deposits and are therefore more difficult to bleach. Also, from recent work on bamboo tissues[13], it appears that lignin in parenchyma cells is more difficult to remove than lignin in fibres. The importance of estimating the porportion of parenchymatous tissue in hardwoods for assessing their suitability for pulp, therefore, needs hardly to be emphasized. In short, woods with little or scanty parenchyma and fine rays are more suited for pulping than those with abundant parenchyma and large rays.

As regards the arrangement and distribution of parenchyma, specially longitudinal parenchyma, one point deserves careful investigation. In some hardwoods like *Butea frondosa* Roxb., *Ficus* spp., *Erythrina* spp., etc., though the amount of parenchyma is high on account of its characteristic stratified arrangement (Figs. 3 and 5), there may be some possibility of devising a method by which parenchyma could be separated from fibre before pulping, as has been done in bamboo.

Size and distribution of vessels—Unlike fibres and parenchyma cells, vessels are not single cells but long vertical, tubular series of cells or segments placed end on end forming a pipe-like structure with profuse pits on their walls. Vessels serve to conduct water and mineral nutrients in the living trees and are found in all hardwoods. They are much larger in diameter than fibres, ranging from less than 50μ to as much as 500μ. In frequency, they may vary from less than 1 to over 50 per sq. mm. The total pore area depends both on the size and the frequency of pores. On account of their structure, vessels appear to be most suited for quick conduction of cooking liquors. The larger the pore area, the easier will be the penetration of liquor.

Tyloses and other inclusions—When pores or vessels are open, the entry of liquids into the wood is greatly facilitated. But sometimes in heartwood they become plugged with foam-like masses, known as tyloses, formed by the protrusion of adjacent ray and parenchyma cells into the vessel cavities. Tyloses are not found in all woods but are characteristic of some, like sal (*Shorea robusta* Gaertn.), garuga (*Garuga pinnata* Roxb.), jhingan (*Lannea grandis* Eng.) and others. Vessels also may become plugged with gummy and other deposits (Figs. 1 and 2) in which case also penetration of cooking liquors is retarded. Obstruction of vessels by tyloses and deposits can be easily made out from gross examination without using the microscope.

Special anatomical features—Among the special features, mention may be made of 'compression wood' in conifers and 'tension wood' in hardwoods.

TABLE 2—CHARACTERISTICS OF HARDWOODS SUITABLE FOR PULP AND PAPER PRODUCTION

Hardwood	Sp. gr.	Colour	Heartwood	Resin canals	Fibres		Parenchyma		Tyloses
					Proportion	Cell wall thickness μ	Longitudinal	Rays	
Echinocarpus spp.	0.32-0.50	Creamy white	Absent or indistinct	Absent	High	2–4	Very sparse	Mostly fine, a few broad	Sparse
Elaeocarpus spp.	0.40-0.60	Sapwood creamy-white	Small, light greyish brown	Absent	High	2–6	Very sparse	Mostly fine, a few broad	Sparse
Duabanga sonneratioides Ham.	0.49	Pale grey to light yellowish brown	Indistinct	Absent	Very high	3–4	Sparse	All fine	Frequently present
Lophopetalum spp.	0.43	Pale yellow to light pink or pale brownish grey	Indistinct	Absent	High	2–4	Somewhat sparse	All fine	Absent
Trewia nudiflora Linn.	0.35	White or cream	Indistinct	Absent	Fairly high	2–4	Fairly abundant	Mostly fine, a few broad	Occasionally present
Tetrameles nudiflora R. Br.	0.34	White or cream	Indistinct	Absent	Moderately high	2–3	Fairly abundant	Fine to broad	Wanting or sparse
Magnifera indica Linn.*	0.59	Light grey to greyish brown	Usually absent, when present very small	Absent	Fairly high	2–5	Sparse to fairly abundant	All fine	Frequently present
Spondias mangifera Willd.	0.37	White to greyish white or pinkish grey	Scarcely distinct	Occasionally present	Moderately high	2–4	Somewhat sparse	Both fine and broad	Not abundant
Lannea grandis Eng.	0.55	Sapwood pale pinkish or yellowish white	Distinct, light to reddish brown	Present	High	2–4	Sparse	Fairly broad	Abundant, all heartwood vessels plugged
Boswellia serrata Roxb.	0.58	Sapwood white or cream	Often distinct, yellowish brown to dark greyish brown	Present	High	3–6	Sparse	Fairly broad	Often present
Garuga pinnata Roxb.	0.60	Sapwood white or cream	Distinct, reddish brown	Present	High	3–6	Very sparse	Fairly broad	Abundant, all heartwood vessels plugged

* Marked tension wood

The presence of appreciable amounts of compression wood in loblolly pine has been shown to lower the strength value of pulp. This is mainly due to the high fibril angle in compression wood. The effect of tension wood in broad-leaved species on pulp quality has not received much attention. Tension wood fibres are typically gelatinous with little or no lignin and a low fibril angle. It would, therefore, be interesting to know, whether the development of tension wood, as often noticed in mango (Figs. 11 and 12) and others, improves the quality of pulp.

Conclusion

Apart from the factors discussed, there are a few others, like submicroscopic structure and chemical composition of cell wall substance, which influence the pulping characteristics of hardwoods. Study of the sub-microscopic structure of the cell wall is a highly specialized field, involving the use of the electron microscope. The variations in the chemical composition of cell walls in different hardwoods and their possible effect on yield and quality of pulp are beyond the scope of this paper. The question of availability of hardwoods, however, is one of importance and deserves special attention from the commercial point of view.

Several investigations have been carried out in the Cellulose and Paper Branch of the Forest Research Institute, Dehra Dun on indigenous cellulosic raw materials (including hardwoods) for production of pulp and paper. The results on performance of 9 species of hardwood for chemical pulp and an equal number for mechanical pulp have been published in a series of publications issued from the Institute. The main difficulty in their utilization appears to be the supply, for in both chemical and mechanical pulping, the raw material should consist preferably of a single species. The obvious way to get over this difficulty appears to be to employ a process in which a mixture of two or more hardwoods, depending on their availability, could be pulped together. Some preliminary trials on semi-chemical pulps from a mixture of salai (*Boswellia serrata* Roxb.), garuga and jhingan have been carried out. More investigations on mixed pulping of hardwood species are necessary to enable reliable conclusions to be drawn.

Based on a consideration of anatomical and other factors, a tentative list of some hardwoods likely to be suitable for pulping has been compiled and their characteristics summarized in Table 2. As far as possible, woods which have otherwise not much demand have been included. The list is by no means exhaustive and serves only to illustrate the scope of the anatomical criteria in assessing the suitability of hardwoods for pulp and paper.

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Discussion

Dr. C. Nanjundayya: I take it, that in paper making, the fibre length of pulp is important.

Shri K. Ramesh Rao: As already explained, marked differences in fibre length as between conifers and hardwoods influence the strength of pulp, but minor fluctuations in fibre length, such as occurring in hardwoods, do not appear to be of much significance (Shri M. P. Bhargava, Chairman, concurred). Fibre wall thickness and cross-sectional area are probably much more important.

Dr. H. Wakeham: It is not possible for the viscose and rayon industry to utilize in some way the useful information given here?

Shri G. C. Sutaria: For the rayon industry, sheet formation is a more important criterion than fibre length.

Shri G. M. Vyas: In the case of hardwood rayon pulps, the sheets tend to break down during steeping. This is probably due to shorter fibres and higher proportion of parenchyma cells.

Shri K. Ramesh Rao: In this connection I suggest that the possibility of first removing parenchyma cells, as has recently been done in bamboo for paper making, may be considered, particularly in hardwoods with stratified parenchyma.

Dr. V. B. Chipalkatti: Is it possible to mix different woods after grinding to obtain better pulp? The reactivity of hardwood pulp can perhaps be increased by pre-mercerizing.

The removal of pith from bagasse is a problem. This problem can perhaps be made easier by adopting a continuous process in which the concentration of alkali would go on increasing through drying by pre-heated steam or air.

Dr. Lavji Thoria: Grinding is a laborious and costly process and economically not feasible. The removal of pith from bagasse is not a problem.

Shri G. M. Vyas: Attempts have been made to increase the reactivity by increasing the total surface available for reaction by shredding wood to match stick size. The pulping time was considerably reduced and the yield increased.

Dr. C. Nanjundayya: If strength is related to fibre length, would not grinding seriously affect the strength of paper?

Shri M. P. Bhargava: The strength of paper depends on the ratio of diameter to length of fibre, bending of fibres, and fibrillation.

Chemical Analysis of Bamboo Tissues

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Cellular constituents, like fibres, parenchyma cells, epidermal and nodal tissues isolated from raw untreated bamboo *(Dendrocalamus strictus)* have been chemically analysed.

Like any other woody material bamboo is not a homogeneous substance. It is composed of tissues which are divided into two broad classes: (i) prosenchymatous tissues (ii) parenchymatous tissues. Long thick-walled fibres arranged in clusters of fibrovascular bundles are the components of the prosenchymatous tissue which gives strength and toughness to bamboo, whereas the parenchymatous tissue is composed of tiny, nearly isodiametric cells whose function is conduction and storage of carbohydrate food material elaborated by plants.

The proportions of these two tissues in the internodes of bamboo vary from bottom to top of the culm and have been recently determined for the first time (Vyas, G. M., Unpublished data). In a *D. strictus* culm of 52 internodes, in which 93 per cent of the total tissue material was in the bottom 32 internodes, the overall average proportion by weight of the parenchyma tissue in these bottom 32 internodes (nodes excepted) was reported to be *c.* 32 per cent varying from 44.5 per cent in the bottom internode to 29 per cent in the thirtieth internode up. Corresponding proportions of parenchyma cells determined by volume on the same culm of bamboo were 68.2 per cent in the third internode to 50.5 per cent in the twenty-sixth internode: the internodes being numbered from bottom upwards. Thus bamboo is considerably heterogeneous and contains large amounts, both on volume and weight basis, of tiny parenchyma cell material. So far, nothing is known to have been published regarding chemical composition of these tissues, nor about their role when bamboo is subjected to various chemical and mechanical treatment.

It is obvious that best utilization of either wood or bamboo would depend on the appraisal of anatomical, morphological, physical and chemical properties of its constituent tissues. In case of pulping, no matter what procedure is used, the final properties possessed by the pulp will mainly depend on the properties inherent in the cellular tissues of the parent raw material. Investigations on varied properties of constituent

tissues of untreated wood have been few because of the difficulty of separating these tissues in pure form from raw wood. In the case of coniferous woods the percentage of other tissues besides tracheids is small. In the case of hardwoods, although the percentage of parenchymatous tissue is appreciable, the separation of the tissues from raw wood is extremely difficult as they are interwoven in both longtitudinal and transverse directions. However, in some instances where a single tissue occupied a fairly distinct area in the structure of wood, it was carefully removed and analysed chemically. In such a manner Harlow and Wise[1] isolated the medullary ray cells of untreated flame-she-oak and white oak by merely scrapping out these cells from thin tangential sections of wood. They were the first to publish the chemical analysis of the ray cells of a hardwood.

In pulp industry a standardized procedure is followed by which a finely divided sample of wood is taken for analysis. The procedure recommended by the Technical Association of Pulp and Paper Industry (T.A.P.P.I.) of U.S.A. consists in comminuting a sample of wood so that all of it passes through 40 mesh sieve, than the fraction of this which passes through 60 mesh but is retained on 80 mesh is taken for chemical analysis. From the viewpoint of pulp and paper technologists this is regarded as representing the chemical constituents of wood, but essentially it may not be so, because some botanical tissues like ray or parenchyma cells might pass out through the 80 mesh screen more or less completely, and hence the sample of wood taken for chemical analysis may not be completely representative of the wood under study. In the case of bamboo it was observed that a considerable portion of the parenchyma tissue passed out of the 80 mesh screen, and hence, the routine chemical analysis of bamboo would not be representative in the true sense.

The fibres and parenchyma cells of bamboo were isolated from the centre portions of the internodes of bamboo by a method involving preparation of thin (*c.* 40 micron) longitudinal sections or shavings of bamboo cut on a microtome, disintegration of these shavings in a small attrition mill or a coffee grinder, and separation of the tissues from disintegrated mixture by flotation in water, when the parenchyma cells floated and the fibre bundles sank to the bottom. The epidermal cells were carefully scrapped off the outside of the bamboo culm by a razor blade. For tissues from nodes, the nodal annuli of an entire culm of bamboo were taken out, finely divided and analysed.

Experimental

Separation of fibres and parenchyma cells—Details about the principal and technique of separation of parenchyma cells from fibrovascular bundles are given below.

Freshly felled culms of 3–5 years age of *D. strictus* were taken for investigation. Tissue samples were separately taken for bottom and top internodes of the culm. For bottom internodes the central portion of the first four internodes from bottom of culm were taken. For upper internodes the central portion of internodes 29, 30, 31 and 32 were used from the same culm which contained in total 52 internodes and wherein the internodes above the thirty-sixth were thin, of solid core and contained little woody material.

For nodal tissues, the nodes of the entire culm excluding the septa in centre of nodes were taken out, crushed in a hammer mill to pass 40 mesh, but the portion from this passing 150 mesh was rejected as it would cause trouble in filtrations during chemical analysis.

To know the comparative values of chemical constituents of the tissues of another species of bamboo, the bottom internodes of a culm of *Bambusa nutans* Wall. were separated into its two constituent tissues and analysed for significant values like lignin, cellulose, ash, solubility, etc.

Preparation of pure samples for analysis—Annulus rings *c* 2 cm. long were cut from central parts of bottom internodes. These were then divided into 4 to 6 segments and aspirated and slightly softened by boiling for about an hour in distilled water. From these segments of internodes radial sections or shavings *c*. 40 micron thick were cut by a knife on a microtome. Alternately, annulus rings could be peeled carefully on a lathe with fine edge of a chisel and tangential shavings so produced could be used in place of radial sections. When these longitudinal shavings were subjected to mild, careful and repeated mechanical disintegrations in a small coffee mill or disc attrition mill, the fibres and parenchyma cells separated out at their middle lamella giving entities consisting solely of fibres or parenchyma cells. The shavings were disintegrated repeatedly till it was observed under microscope that the cleavage between the tissues was complete. The tissue mixture was then sieved through 30 mesh and the portion passing 30 mesh was passed through 150 mesh. The portion passing 150 mesh was rejected as it would create difficulties in filtrations during chemical analysis. The portion between 30 and 150 mesh was dried in an oven and was then spread over water in a shallow dish; when the fibrous portion sank down and the parenchyma cells being lighter floated on the surface of water; these were then taken out. Both the portions were filtered, dried and separately refloated on the surface of water to remove impurity of one tissue in the bulk of the other. Three to five such flotations gave pure samples of the tissues.

Separation of tissues in quantity from the upper internodes was difficult. The internodes were thin and could not be handled properly on the microtome for cutting sections. Besides, the distribution of tissues in the top internodes is fairly close and hence complete cleavage

TABLE 1—CHEMICAL ANALYSIS OF FIBRES AND PARENCHYMA CELLS OF BAMBOO

(Percentage values based on dry weight of tissue material analysed)

Constituent	*DENDROCALAMUS STRICTUS*			*BAMBUSA NUTANS*	
	Bottom internodes		Upper internodes	Bottom internodes	
Solubility in:	Fibres* %	Parenchyma cells %	Fibres* %	Fibres* %	Parenchyma cells %
Cold water	0.76	1.14	1.03	0.22	2.68
Hot water	3.75	4.26	3.12	1.07	2.86
NaOH, 1%	12.58	21.30	17.81	18.78	25.0
NaOH, 7.14%	23.89	23.30	24.92	n.d.	n.d.
Ether	0.05	0.05	0.33	0.23	0.54
Alcohol-benzene	1.18	1.66	0.88	0.47	1.65
Ash	0.71	1.27	1.35	0.48	0.97
Cellulose‡	63.23	51.33	61.41	66.33	53.43
Lignin	28.66	27.27	23.30	24.75	25.78
Pentosans	15.18	19.67	19.42	20.41	20.64
α-cellulose	53.93†	39.35†	46.62	52.5	40.2
β-cellulose	5.78	7.68	6.59	n.d.	7.96
γ-cellulose	3.50	4.35	8.20	n.d.	5.29
Pentosans in cellulose‡	12.09	9.91	12.17	9.0	7.90

* Contained vascular tissue

† Alpha from fibres contained 4.16% pentosans, and alpha from parenchyma cells contained 1.12% pentosans

‡ Cross and Bevan

n.d.—not determined

was difficult. The upper internodes also contained larger amounts of 'cap fibres' which were thin-walled and which floated along with the parenchyma cells. In these circumstances, only the fibres which formed greater proportion of the tissue mass in the upper internodes were separated by the procedure outlined above and chemically analysed.

Careful peeling of epidermis of the bamboo stem by a razor blade gave a material composed of small, nearly isodiametric cells which on examination under the microscope showed globular incrustations within the cells. A fresh bamboo culm having 50 internodes gave 20 g. of this tissue which amounted to *c.* 0.2 per cent of dry weight of the bamboo culm. Even with best effort, the presence of subepidermal layer (which was also parenchymatous) in the sample for analysis could not be avoided.

The tissue distribution is very complex in the nodes as the fibre strands run in all directions. Consequently the separation of the tissues in pure form was difficult, and as stated before the entire nodal annuli were crushed in a hammer mill and the portion passing 40 mesh and retained on 150 mesh was chemically analysed.

Methods of chemical analysis—Water solubles, alcohol-benzene and ether extractives, Cross and Bevan cellulose, lignin, alpha-, beta-, and gamma-cellulose and ash were determined by Bray's methods[2]. Pentosan content and holocellulose were determined using T.A.P.P.I. methods. Methoxyl content both in the tissue and in their Klason lignins were determined by T.A.P.P.I. standard method with the alteration that the methyl iodide formed was absorbed in alcoholic silver nitrate and determined gravimetrically as silver iodide.

Results and Discussion

Results of chemical analysis of fibre and parenchyma tissues are given in Table 1. Table 2 contains a detailed analysis of tissues of the epidermal layer and the node annuli. Tables 3 and 4 give the holocellulose and methoxyl contents of the tissues of bamboo.

The heterogeneous character of the cellular constituents of bamboo is fully reflected in the chemical analysis of these tissues.

Water and alkali solubles—The parenchyma cells in general contained higher alkali and water solubles than the fibres. The comparatively high value of the water solubles obtained for the epidermal tissue and the nodal tissue is partly due to the fact that prior to separation these tissues were not boiled in water. The exceedingly high value of alkali solubles for the epidermal tissue which is parenchymatous are noteworthy.

Organo-soluble extractives—Hatch[3] has reported that the ray cells of some woods contain ten times as much alcohol-benzene extractives as the tracheids. In the case of bamboo the ether and alcohol-benzene

TABLE 2—CHEMICAL ANALYSIS OF TISSUES OF EPIDERMIS AND NODE ANNULI OF *DENDROCALAMUS STRICTUS*

(Percentage values based on dry weight of tissue material analysed)

Constituent	Tissues of epidermis *Mean %*	Tissues of node annuli *Mean %*
Solubility in:		
Cold water	11.44	6.53
Hot water	14.00	10 00
NaOH, 1%	63.29	25.07
NaOH, 7.14	69.37	33.74
Ether	9.13	0.40
Alcohol-benzene (1:2)	17.56	4.34
Ash	27.64	2.02
Cellulose*	42.82 (with ash)†	55.34
Lignin	40.15 (with ash)‡	27.35
Pentosans	11.78	16.67
α-cellulose	..	34.85
β-cellulose	..	11.69
γ-cellulose	..	8.80
Pentosans in cellulose*	..	11.73

* Cross and Bevan

† Cross and Bevan cellulose value after deducting ash is 27.87%

‡ Lignin value after deducting ash is 14.29%

extractives are fairly low except in the case of epidermal tissues which appear to be waxy. The values of ether and alcohol-benzene extractives for the usual 60–80 mesh fraction of bamboo substance are higher than what are obtained for the individual parenchyma and fibre tissues in the present case. The reason may probably lie in the fact reported by Sutezo[4] that bamboo yielding 13.52 per cent matter soluble in water had of this 10.05 per cent (% based on bamboo weight) soluble in alcohol. Hence it is presumed that some organo-soluble matter was removed during the preliminary softening of the internode pieces in boiling water.

Ash—The parenchyma cells, node annuli and the epidermal tissues contain larger amounts of ash than the fibres. The portion of the parenchyma tissue which passed through 150 mesh screen and which was not taken into the sample for analysis contained a high ash content

of 6.14 per cent. The ash (exceptionally high, 27.7%) of the epidermis of bamboo consists of 97.7 per cent silica.

Cross and Bevan cellulose—Both in *D. strictus* and *B. nutans* the cellulose was *c.* 12 per cent higher in fibres of the bottom internodes than in the corresponding parenchyma cells. The cellulose in the fibres contained somewhat more pentosans than the cellulose in the parenchyma cells. The fibres of upper internodes contained slightly less cellulose than the fibres of the bottom internodes.

Lignin—Harlow and Wise[4] have reported that the ray cells of the Australian white oak and flame-she-oak contain more lignin than the entire wood substance. The differences observed in the lignin contents of the fibre and parenchyma tissues are small and may be due to experimental error. Keito[5] showed that top portions of a bamboo stem (divided equally as top, middle and bottom) contained one third the lignin found in the bottom portion of the stem. In the present case it has been found that lignin in the fibre tissue of the upper internodes is 5.36 per cent less than in the same tissue of the bottom internodes.

Alpha-cellulose—The higher values of Cross and Bevan cellulose in fibres over the parenchyma tissue are reflected to an equal extent in the alpha determination from their celluloses. Fibres are a more alpha-yielding tissue than the parenchyma cells, but at the same time

TABLE 3—HOLOCELLULOSE CONTENTS OF *DENDROCALAMUS STRICTUS* FIBRE AND PARENCHYMA TISSUES

Tissue	Alcohol: benzene (1:2) soluble %	Holocellulose on extractive free basis %	Holocellulose on raw tissue* %
Fibres	1.18	73.55	72.68
Parenchyma cells	0.67	67.66	67.20†

* Values not a part of summative analysis

† Cross and Bevan cellulose from the same sample of parenchyma cells is 52.62%

TABLE 4—METHOXYL CONTENTS OF *DENDROCALAMUS STRICTUS* TISSUES* AND THEIR LIGNINS

Tissue	Lignin %	Methoxyl content %	Methoxyl content on lignin, %	
			Found	Calculated†
Fibres	27.25	4.69	16.79	17.95
Parenchyma cells	27.37	5.12	16.11	18.71

* Tissues separated by flotation method from bottom internodes No. 2 and 3

† On the basis that all the methoxyl is contained in the lignin which may not be correct

the alpha from the fibres contains somewhat more pentosans than the alpha from parenchyma cells.

Pentosans—The fibres of the bottom internodes contain 4.5 per cent less pentosans than the parenchyma cells, whereas the fibres of the upper internodes contain as much pentosans as contained in the parenchyma of bottom internodes. On the other hand in case of *B. nutans* the fibres and parenchyma cells of bottom internodes contain the same amount of pentosans.

Methoxyl contents—In general the methoxyl content of the lignins from hardwoods is reported to be 20–22 per cent and of softwoods, 14–16 per cent. Sutezo and Muneo[6] found that the methoxyl content of glycerol lignin from bamboo (extracted by 25% glycerol at 150°C. for 4 hr. at *p*H 9) was 13.96 per cent which corresponds to the methoxyl content of softwoods. Azami and Sengoku[7] also found that the methoxyl content of lignin in bamboo is rather low compared to the hardwood lignins and is near the value of softwood lignins. Recently Aggarwala[8] and McCarthy determined methoxyl content in bamboo (*D. strictus*) and found the value to vary from 4.60 to 4.28 per cent on the basis of extractive free bamboo. They found a high Klason lignin value of 34.6 per cent. So, if all the methoxyl was assumed to be associated with lignin, which is not necessarily correct, bamboo lignin according to these authors would contain 13.2 per cent methoxyl, which is a value corresponding to softwood methoxyl contents. In the present evaluation of the methoxyl contents of the lignins of the parenchyma and fibre tissues it was found that the values were 16.11 and 16.79 per cent methoxyl.

Summary

The fibres, in the bottom internodes of the culm of *Dendrocalamus strictus* Nees, contained 11.9 per cent more cellulose, 1.4 per cent more lignin and 14.6 per cent more alpha than the parenchyma cells; whereas the latter contained 4.6 per cent more pentosans, more solubles and extractives than the former. The fibres of top internodes contained less lignin and cellulose than the fibres of the bottom internodes. The epidermal cells contained large amounts of extractives and *c.* 28 per cent ash which was mostly siliceous. Nodal tissues contained more solubles and a little more ash than the internodal tissues.

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Discussion

Shri M. P. Bhargava: Do you have a satisfactory method for separating the fibres and parenchyma cells from bamboo?

Shri G. M. Vyas: Yes. This can be easily done by mechanical means and the Council of Scientific & Industrial Research has taken 2 patents (Indian Patents No. 49054 and 57267) for this process.

Dr. P. K. Choudhury: Have you determined the differences in ash content in the top and bottom internodes?

Shri G. M. Vyas: There are various difficulties involved in a precise determination of this type. However, top internodes have higher ash content than bottom ones.

Optimum Digestion Conditions for Production of Strong Bamboo Pulps—A Preliminary Study

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Preliminary investigations on the digestion of bamboo for the commercial production of bamboo pulp indicate that the use of 8 per cent concentration of active chemicals in sulphate cooking liquor and impregnation of bamboo chips with cooking liquor pre-heated to 170°C., result in pulp yields higher than those obtained by the conventional processes of digestion ; besides, the total cooking cycle is reduced.

Kraft wrapping paper is being manufactured in one of the Indian paper mills from 100 per cent bamboo pulp. The strength properties (burst and tensile) of the paper, however, do not compare favourably with those of imported kraft paper.

Recent enquiries point to the use of partially decayed bamboo, resulting from fungi and borer attacks in forests and mill yards, as a contributory cause for the comparatively poor strength of kraft paper made therefrom. Detailed investigations on the subject are proposed to be taken up shortly. Meanwhile, studies have been undertaken to determine the optimum conditions for the digestion of bamboo for the commercial production of pulp possessing high strength properties. This paper is a preliminary report on the study of the effect of employing, in sulphate cooking, chemicals in concentrations higher than are ordinarily employed in commercial practice, namely, 4–5 per cent active alkali as sodium hydroxide, which apparently results in the production of weak bamboo pulp.

Experimental Procedure

Dendrocalamus strictus (salia) from Palamau Forest Division, Bihar was used in these experiments. A mixture of 2 and 3 years old culms, free from fungal and borer attacks, was obtained, soaked in water for about a week to remove soluble sugars, dried in air, and cut manually into ¾—1 in. chips. The percentage of moisture in the chips was determined for each charge.

A stainless steel cylindrical rotary autoclave of 5-litre capacity was used for digestion. The autoclave was electrically heated and fitted with an automatic thermocouple regulator, temperature gauge, pressure gauge and safety and blow-off valves. Each charge of chips consisted of a quantity equivalent to 600 g. of bone-dry chips. Cooking liquor containing the requisite quantity of alkali (caustic soda and sodium sulphide) was pre-heated before charging into the autoclave so that the maximum cooking temperature was attained in *c.* 30 min. As sodium sulphide was not available, powdered sulphur (3% of the wt. of bone-dry chips) was used with caustic soda liquor for digestion.

Digestions were carried out at two steam pressures and temperatures commonly employed for large scale digestion of bamboo, namely 80 lb./sq. in. equivalent to 162°C. and 60 lb./sq.in. equivalent to 153°C. The ratio of cooking liquor to bamboo chips (bone-dry) was varied from 4:1 for 5 per cent concentration to 3:1 for concentrations ranging from 8–12 per cent in order that the percentage of active alkali in the charge may not be excessive. It was found that liquor to chip ratio of 3:1 was the lowest that could be employed for digestions in the autoclave; a lower ratio resulted in an unduly high percentage of screenings and consequently lower screened yield. In large scale digesters with effective and efficient forced circulation of cooking liquors, it should be possible to have a liquor to chip ratio of 2–2.75:1, particularly if indirect heating is adopted. Thus to digest bamboo with 8 per cent concentration cooking liquor, the requirement is 16–22 per cent (av. 19%) sodium hydroxide on bone-dry weight of bamboo, and not 24 per cent as was found necessary in the laboratory digestion.

The actual digestion period (time at the maximum cooking temperature) was kept constant at 1½ hr., since longer periods resulted in lower screened yield. For concentrations of 10 and 12 per cent, the digestion periods were 1¼ hr. and 1 hr. respectively in order to avoid overdigestion and lower screened yield.

At the end of the digestion period, the autoclave was relieved to atmospheric pressure and the entire charge pressed in a tincture press to separate the black spent liquor from the pulp. The pulp was given a further hot wash in the tincture press and then washed first with fresh water on 8 mesh sieve to screen out uncooked or partially cooked pieces and then on 60 mesh sieve until free from traces of alkali. The percentage of moisture in the washed pulp and the percentage yield of pulp on bone-dry bamboo was calculated.

Results

For determining the strength (burst and tensile), samples of pulp were beaten in a 1½-lb. Niagara experimental beater according to the T.A.P.P.I. standard method T 200 m45. Measured samples of pulps

were taken out from time to time as the beating progressed, disintegrated and made into wet sheets, and dried under standardized conditions on a sheet making machine obtained from Ernst Haage, Germany. Bursting and tensile strengths of the sheets were then determined on Perkins Mullen tester and Schopper tensile strength tester, both electrically driven, in accordance with the T.A.P.P.I. standard method T 403 m53 and T404 m50. The results of several digestions and strength tests carried out on the sheets are given in Table 1.

Digestions have also been carried out with sulphate cooking liquor of 8 per cent active alkali concentration—a concentration which, as seen from Table 1, has given the best result as regards yield and strength properties—to find out if pulps could be produced which would bleach with 8–10 per cent chlorine by the multi-stage bleaching process to a high bright shade and, at the same time, possess higher strength properties than ordinarily found in easy bleaching pulps, produced conventionally in Indian mills either by the Fractional or the Overhead method for the manufacture of bleached writing and printing paper. The results of digestions are set out in Table 2. The strength properties of the pulps have not been determined or compared with those of conventionally produced pulps.

It will be seen from Table 1 that by increasing the concentration of chemicals in the cooking liquor from 5 to 8 per cent, the screened yield of pulp has been increased. However, from 10 per cent concentration upwards, the screened yield begins to fall, even though the period of digestion is reduced.

As regards the development of strength on beating, it will be seen from Table 1 that the pulp obtained with 8 per cent concentration cooking liquor develops higher strength properties on beating than pulp obtained with lower concentration cooking liquor. The pulps obtained in cooks No. 70–72, when beaten to about 60° SR, possess a burst factor of about 60 and a breaking length of *c.* 8,000 metres. These strength properties are further improved by the removal of cells and fines from screened pulp by prolonged washing of pulp on a 60 mesh sieve and beating the pulp in the experimental beater under standard conditions (cooks No. 71 and 72, Table 1). The strength properties developed by beating the pulp free from cells and fines, namely, burst factor of 66 and breaking length of 9,732 metres, compare favourably with the strength properties of a Swedish kraft pulp (Patria kraft sulphate pulp) which is reported to have a burst factor of 62 and a breaking length of 9,600 metres at 45° SR. The elimination of cells and fines from bamboo pulp, while advantageous from the point of view of strength development, reduces the percentage yield on raw material quite appreciably. In pulps produced from *D. strictus,* the percentage of cells and fines is *c.* 20 or even more. It is proposed to conduct further studies on the effect of cells and fines on final screened yield of pulps and on their beating characteristics.

TABLE 1—DIGESTION CONDITIONS AND BURST AND TENSILE STRENGTH OF PULPS

Cook No.	Digestion conditions: Active alkali as NaOH on chips %	Conc. of active alkali as NaOH %	Max. temp., °C.	Max. pressure lb./sq. in.	Period at max. cooking temp., hr.	Screened pulp yield on chips %	Strength: Freeness of beaten pulp (Schopper-Riegler degrees)	Substance of sheet g./sq. m.	Burst factor	Breaking length m.
40 & 41	20	5	162	80	1½	37.8	40	61.5	43.3	6,830
							45	60.0	49.2	7,110
							60	61.8	51.8	7,551
							70	62.4	54.3	7,553
							76	57.3	63.5	8,284
43 & 44	21	6	162	80	1½	39.1	42	60.0	46.6	6,444
							65	60.0	55.6	7,000
							74	60.0	59.1	7,778
48	24	7	162	80	1½	41.1	40	59.4	41.7	6,622
							50	58.5	44.4	6,838
							60	57.0	50.7	7,017
							76	57.0	56.0	7,485
83 & 84	24	8	162	80	1½	44.8	44	61.1	42.1	7,464
							56	61.5	55.1	7,262
							75	59.1	59.3	7,612
81 & 82	20	5	153	60	1½	45.2	47	61.7	47.4	6,760
							58	62.0	51.5	7,569
							74	62.8	52.7	7,623
79 & 80	21	6	153	60	1½	45.7	41	62.0	43.7	5,637
							57	62.5	50.4	7,144
							70	61.2	52.7	7,813
85 & 86	21	7	153	60	1½	44.3	42	63.6	44.2	6,236
							62	63.3	52.9	6,851
							72	63.7	57.2	7,745
70 & 71	24	8	153	60	1½	45.6	39	58.7	46.5	7,384
							57	61.3	58.5	8,098
							71	59.7	62.0	7,900
71 & 72	24	8	153	60	1½	45.5	50	61.6	63.3	8.644*
							70	60.8	66.3	9,732*
63–65	30	10	153	60	1¼	41.0	†	†	†	†
67 & 68	36	12	153	60	1	38.4	†	†	†	†
Factory pulp	21	7.6	156	75	4	39.0	39	55.0	41.7	6.679
							57	63.0	45.9	6.032
							57	66.0	42.6	6.306
							66	61.0	54.0	7,663

* Pulp almost free from cells and fines

† Strength properties not determined as yields were rather low

TABLE 2—DIGESTION OF BAMBOO FOR BLEACHABLE PULPS

Cook No.	Active alkali as NaOH on chips %	Conc. of active alkali as NaOH %	Max. cook. temp. °C.	Max. cook pressure *lb./sq.in.*	Cooking period at max. temp. *hr.*	Yield of pulp on chips %	% Chlorine on screened unbleached pulp
81–82	20	5	153	60	1½	45.2	14.7
79–80	21	6	153	60	1½	45.7	13.4
85–86	21	7	153	60	1½	44.3	12.7
72	24	8	153	60	1½	46	12.4
73	24	8	153	60	2	44.8	11.2
74–76	24	8	153	60	2½	45.4	9.5
77–78	24	8	153	60	3	43.2	9.3
25	22.5	5	153	60	2	39	7.5
			162	80	1		

It has been mentioned earlier that a digestion period of 1½ hr. was found to be optimum from the point of view of the percentage yield of screened pulp. It was also found in the course of the investigation that the short period of 1½ hr. was adequate only when the time required to attain the maximum cooking temperature was short, e.g., 30 min., giving a total cooking cycle of 2 hr. A longer total cooking cycle seems to adversely affect not only the percentage yield of screened pulp, but also the strength development properties, even though the concentration of chemicals in the cooking liquor may be as high as 7–8 per cent. This may be seen from the results of strength tests (Table 1) on a sample of bamboo kraft pulp produced in the factory. The temperature and pressure raising period and, therefore, the total cooking cycle, may be shortened to get the full advantage of higher concentration of chemicals in cooking liquors by bringing the charge into contact with cooking liquor pre-heated to *c.* 170°C. in a separate vessel (Indian Pat. No. 51869, 1954).

The results of digestions carried out with the object of preparing bleachable bamboo pulp (Table 2) show that the yields of screened pulp bleachable to a good white shade by the multi-stage bleaching method, with *c.* 9.5 per cent chlorine on pulp, is much higher when the concentration of chemicals in the cooking liquor is 8 per cent than that obtained by the conventional method of cooking (cook No. 25, Table 2). Investigations on the subject are in progress.

Conclusion

Investigations carried out hitherto indicate that the use of 8 per cent concentration of active chemicals in sulphate cooking liquors and impregnating bamboo chips with cooking liquor pre-heated to *c.* 170°C., result in higher yields of pulps than those normally obtained by the conventional processes of digestion and also in a reduction of the total cooking cycle. The pulps obtained develop fairly high burst and tensile strength properties on beating and are suitable for the manufacture of strong packing and wrapping papers. The pulps are bleachable to a good white shade by the multi-stage bleaching process and may be utilized for the manufacture of various types of printing and writing paper.

Discussion

Dr. P. K. Choudhury: Why do you think that 1 in. chips would give the best results?

Shri M. P. Bhargava: In large scale trials we have found that chips of ¾–1 in. length give the best results. This is a compromise between increasing the total surface for reaction and the cost of shredding to very fine size.

Shri G. M. Vyas: Are commercial shredders available for getting 1 in. chips?

Shri M. P. Bhargava: Various types of chippers are available for this purpose.

Dr. Lavji Thoria: A combination of crushing and chipping may prove advantageous.

Shri M. P. Bhargava: It certainly would be if it was practicable. With bamboo stems the difficulty is that after crushing, they become so flexible that uniform chipping is not possible. Crushing after chipping is not at present practicable.

Evaluation of Viscose Grade Pulp

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The characteristics of a viscose grade pulp in terms of its chemical composition and physical properties, such as alpha-, beta- and gamma-cellulose, non-cellulosic polysaccharides, extractives, inorganic impurities, disperse viscosity, etc. only partially define its suitability for conversion to viscose. Hence, it is necessary to examine additional properties, such as nature and morphology of tissues, accessibility, degree of polymerization and polydispersity, sheet structure, and swelling. Besides, the degree of filtrability of the viscose solution made from it is also an important criterion for evaluation.

The problem connected with preparation of viscose grade pulps from new and untried cellulosic raw materials are many and have so far defied solution in India. Among the indigenous cellulosic raw materials available for such refined pulps, bamboos, reeds and agricultural residues form the ultimate choice, because they are the only ones sufficiently available in India. These raw materials, and particularly bamboo have not been processed hitherto on a large scale into viscose grade pulps and are known to present problems not so far met with in any similar endeavour. Other problems are basic to the viscose pulp industry and arise from the lack of definite criteria for viscose grade pulps.

The significance attached to the values of alpha-cellulose, pentosans, disperse viscosity, degree of polymerization, ash, etc. does not hold equally for coniferous and deciduous wood pulps, nor for pulps prepared by different processes from the same raw material. These values, have, in the light of the present knowledge, only empirical significance and help to catalogue the pulps by eliminating those which do not satisfy certain minimum needs with respect to chemical composition. The recent trend is to lay emphasis on a basic understanding of the physical properties and the chemical constituents of cellulose in relation to the structure of cell wall, molecular properties of cellulose, crystalline and accessible areas of cellulose matrix, reactivity, cross bonds, drying and swelling behaviour, structure of the dissolved ester and behaviour of the aggregates of xanthate during filtration and spinning. However, evaluation on the basis of such a large number of tests is not practicable, and in general, the dissolving pulp in question is subjected to a study of processing behaviour when it is made into viscose and spun into yarn on a miniature scale.

Testing for Viscose Pulps

Facilities for such small scale processing and evaluation of viscose pulps are, to our knowledge, not available in India at present and pulps are required to be sent abroad for testing. This is time-consuming and further the significance of particular evaluation tests is not always clear. Hence, it would be useful to review, in the light of available knowledge, what important characteristics define viscose grade pulps, what are their limitations, and which aspects of the evaluation have a bearing on the physical and chemical characteristics of cellulose.

Qualities of Acceptable Cellulose

The manufacture of viscose rayon involves the conversion of cellulose, to its ester derivative, dissolution of this ester in alkali and spinning and regeneration of the dissolved ester back to cellulose threads. Cellulose has to be considerably degraded from its fibrous solid phase before it can be dissolved and spun into a reconstituted, thread-like system of fibrous structure. The chemical cellulose undergoing this change has to conform to certain rigid processing requirements and quality. The problem is to understand the qualities of the acceptable cellulose so as to assist the pulp manufacturer in developing cellulose from new indigenous raw materials.

It is well known that cellulose should be free from all non-cellulosic carbohydrates and should have a high alpha value. But alpha is not exclusively cellulose except in very special cases (e.g., purified cotton). It is an arbitrarily defined fraction of cellulose pulp and does not indicate a definite chemical substance, nor is it characterized by a definite type of structure. The terms alpha-, beta-, and gamma-cellulose are indefinite in their components and vary widely depending upon the processing history and the raw material from which the pulp is made. Alpha-cellulose is also not indicative of the chain length of cellulose, as it is possible to have 98 per cent alpha with a disperse viscosity which corresponds only to 200 to 300 glucose units[2].

The original intention of Cross and Bevan in introducing alpha value was to measure the amount of cellulose resistant to mercerizing by caustic alkali[3], but a dilution stage introduced in the procedure by changing the concentration of caustic from 17.5 per cent to half its value brings about an increased solubility of cellulose. More recent methods published in Canada[4] and introduced as a standard by the Swedish pulp and paper industry[5], avoid this change in concentration of caustic and on this account give a more fundamental value than the original alpha test of Cross and Bevan. These new methods are volumetric in character and determine the alkali-resistant cellulose without any change in concentration of caustic throughout the procedure. When 21.5 per cent caustic is used, the result is claimed

to be equal to rayon yield in viscose process, and when 10 per cent caustic is used, it determines the cellulose resistant to caustic of maximum solubility, and this latter value is of the same order of magnitude as the conventional alpha-cellulose, but is of more fundamental significance.

Increase in alpha is an improvement in fibre quality which may be incidental to other qualities, such as removal of pentose groups or swelling in mercerizing caustic. In general, pentosans of the sulphite pulp are largely extracted by mercerizing in alpha estimation, but pentosans in a sulphate pulp are resistant to alkali extraction in mercerizing caustic, especially when the base raw material is hardwood.

From the point of view of physical structure, alkali insolubility of cellulose in the mercerizing liquor used in alpha determination is based on the presence and size of three-dimensional units and on the strength of bonds that tie adjacent chains of cellulose to one another[2]. Differences in alpha value of the same raw material processed by different pulping techniques, like sulphite and sulphate, are explained on the basis of difference in crystallinity or crystalline pattern of alpha-cellulose or by partial cross bonding of cellulose and hemicellulose chains. Thus the physical and chemical properties of the fibre will depend on the structure of alpha-cellulose. In such a case, crystal size, number of oriented chains in the crystalline region, and the way in which the crystallites are interspersed in the non-crystalline region may be important. So far no relationship has been found to exist between the alpha-cellulose value and accessibility, because high alpha and low accessibility (e.g., cotton) and low alpha and low accessibility (e.g., hydrolyzed cotton) could be produced at the same time[2].

Role of pentosans—In the cellulose produced from wood, non-cellulosic carbohydrate impurities are always present. The hexosans (glucosans, mannosans, galactosans, etc.) predominate in the hemicelluloses of coniferous woods which also contain some pentosans (xylan), while the hemicelluloses of deciduous woods, straws, bamboos, etc., consist mainly of pentosans (xylan). The presence of pentosans in viscose grade pulps from hardwoods raises a number of problems associated with the formation of resistant pentosans in alkaline pulping, such as low degree of polymerization of pentose residues, varied response of pentose groups in steeping and xanthation, and low filtrability of pulps containing pentosans.

Pre-hydrolysis of wood has proved useful in the removal of pentosans from hardwood pulps. It is possible to prepare reactive viscose grade pulps containing low pentosans, low ash and high alpha-cellulose by inclusion of pre-hydrolysis in the pulping technique. But pre-hydrolysis also de-activates lignin and degrades cellulose at the same time. Depending upon the conditions of pre-hydrolysis, the alpha passes through a maximum, and with more severe pre-hydrolysis, alpha is

degraded. Often with severe pre-hydrolysis, pentosans, alpha-cellulose and yield are lowered at the same time. For example, pre-hydrolysed bamboo pulp with a low yield (23.8 %) and containing 3 per cent pentosans lost 16.96 per cent alpha in an effort to remove 17.6 per cent pentosans (not taking into account the pentosans contained in alpha)[6]. Thus the pre-hydrolysis technique of pentosan removal requires a thorough study for the particular raw material in question.

In general, pre-hydrolysis lowers pentosans, increases alpha, and improves reactivity in the case of sulphate pulps. This type of hydrolytic action is necessary in order that the fibres may disintegrate in the direction transverse to the fibre axis which opens up the fibre structure and facilitates the penetration of carbon disulphide during xanthation[7]. Recently, some workers subjected sulphate pulps to post-chlorination hydrolysis, followed by alkali extraction, and found that pentosans could be sufficiently lowered without undue loss of alpha[8, 9]. It is reported by some Japanese workers[10, 11] that a rayon grade pulp from *Pinus densiflora* produced by sulphate cooking, followed by post-chlorination hydrolysis and alkali extraction, gave a pulp in good yield with 91–92 per cent alpha-cellulose and 700–800 D.P. (degree of polymerization) which compared well in filtrability with pre-hydrolysed pulps and, at the same time, the spinnability and quality of the filament were not affected.

Although the role of pentosans in the xanthation and filtration steps is not clear, there is no doubt about the advantages gained by the removal of pentosans[8]. The deleterious effects of high pentosan content are: contamination of steeping liquor, uneven xanthation (as pentosans presumably take up carbon disulphide and prevent xanthation of the inner layers of cellulose fibre), low filtrability due to unreacted cellulose, and low strength of rayon yarn because of the presence of pentosans up to the yarn stage.

Inorganic impurities and their removal—In pulps from bamboos, reeds and agricultural residues, the ash, and particularly silica, is retained in large amounts. Except silica, other ash constituents can be removed by some kind of hydrolytic treatment. Marschall[12] found that the filtrability deteriorated with higher ash content, particularly silica. On the other hand, Vuori[13] found that ash constituents containing sodium ions have no deleterious effect on filtrability. Samuelson[14] found that the clogging constant increased with increase in the silica content of sulphite pulp (silica added from outside) and for acceptable filtrability (clogging constant, 50), the silica content should not be more than 0.025 per cent.

Disperse viscosity—Next to non-cellulosic constituents, the viscosity of pulp is an important characteristic as it is related to the degree of polymerization of cellulose. Rayon pulp should have a narrow molecular weight distribution curve, but the extent to which the properties of the final yarn depend upon polydispersity has not been found out. The

pulp suffers considerable degradation in ageing and also, to some extent, in ripening.

Uniformity—Pulps from hardwoods and agricultural residues wound contain considerable and varying amounts of ray or parenchyma tissue elements. There are wide differences in the morphology and cell patterns of such tissue elements. With respect to chemical constituents, ray and parenchyma cells of hardwoods are known to contain higher pentosans, lower alpha, lower D.P. cellulose, and higher amounts of ash and extractives than fibres[15]. Perila and Roschier[16] showed that parenchyma cells separated from aspen and fir pulps contained less alpha and pentosans, but more resin, ash and lignin, and that parenchyma cells did not xanthate well. Le Rollen[17] stated that parenchymatous cells of beech sulphite pulp have unusually high swelling capacity and their presence tends to give yarn of low tensile strength. Recently considerable work has been done on the role of parenchyma cells in bamboo pulping and methods have been proposed to separate out these cells from bamboo[18, 19]. In general, the role of parenchyma cells in dissolving pulps from hardwoods, bamboo, reeds, etc., requires careful evaluation with respect to swelling ability, xanthation reactivity and strength properties of rayon yarn produced from such pulps.

When pulps are prepared so as to obtain high alpha, low pentosans, and even chain length distribution, the micellar and crystalline structure of cellulose undergoes considerable changes. In this context, the purpose of pre-hydrolysis seems not only to lower the pentosan content, but at the same time, to open up the fibre structure, break up the larger crystallites which are then more readily penetrated by the hot alkaline pulping liquors as well as by the swelling and depolymerization reagents used during the process of xanthation. In short, the severe pulping and purification conditions adopted in the preparation of viscose grade pulps seem to have the ultimate object of increasing the accessibility or the reactivity of cellulose chains to swelling and xanthation reaction.

It would be apparent that the chemical composition of viscose grade pulps does not definitely indicate that the pulp would be reactive towards xanthation, whereas the physical properties, like accessibility, swelling, presence of cross bonds and sheet structure, are difficult to measure and have so far not been correlated to the processing behaviour of the pulp in viscose making. Presently, the evaluation of a viscose grade pulp is confined to the study of its behaviour during a trial xanthation and filtrability value of dissolved xanthate.

According to Heuser[20], the question, basic to a good suitability method is, what makes a good and bad filtering viscose. Similarly Jayme and Chen[21] point out that none of the usual analytical characteristics including the D.P. of pulp made by different processes are sufficient in itself for predicting its suitability for viscose manufacture. The reactivity

concept as applied to pulp for viscose manufacture reduces itself essentially to the filtering properties of viscose prepared therefrom. Various authors have studied the filtering properties of viscose grade pulps from many angles. Samuelson contributed a series of papers[14, 20-26] bringing out the importance of filtrability determination in viscose pulp evaluation. Klauditz and Berling[27] investigated the filtrability of viscose with respect to the morphological properties of pulps. Vosters[28] studied the strength properties of isotropic xanthate filaments with respect to the filtering properties of pulp. Vuori[29] studied the correlation between the filtering properties and the polydispersity of pulps. Marschall[12] investigated those significant variable of pulps, and their processing which affect filtrability.

In fact, the estimation of filter value is an evaluation of the structural properties of viscose, because the shape, size, number, mobilities and behaviour of xanthate aggregates which constitute the structure of viscose solution, determine whether the viscose is filtrable or not. Filtrability is then a study of the state of solution of viscose. Previously the clogging of filter pores during filtration of viscose solution was mainly attributed to the undissolved residues and suspended impurities which formed a cake on the filter medium. Bergek and Ouchterlony[30] have shown that clogging of the filter cannot be caused solely by undissolved bodies suspended in viscose solution. In support of this, they found that after repeated filtration of a viscose solution, followed by relaxation time, the clogging constant which is a measure of the clogging components remains unchanged. They are of the opinion that filter clogging is caused mainly by the aggregated particles of cellulose xanthate which break up during filtration and recombine into aggregates after filtration.

Hermans and Bredee[31] have given a detailed mathematical treatment of the mechanism of constant pressure filtration of viscose solution. They consider the filter medium to be made up of a set of parallel capillary tubes of constant length, the diameter of which decreases gradually and regularly by the adsorption of particles against the walls of the tube in such a way that the inside volume decreases proportionally to the volume of filtrate passed through. In such a case, filtration at constant pressure is governed by the expression :

$$kt/_2 = t/v - 1/s_o$$

where t is the time in minutes in which volume v in cc./sq. cm. filtering surface is filtered, S_0 is initial rate of flow and k is called the filtration constant. Another convenient form in which the standard law of Hermans and Bredee is often expressed is :

$$K = \frac{\text{constant } (t_2/v_2 - t_1/v_1)}{t_2 - t_1}$$

where K is called the clogging constant.

Various methods are available for measuring the filtrability of viscose solutions. The method of Jayme and Chen[21] consists in measuring the amount of fibrous residue that remains when viscose solution is centrifuged. This method works well when the pulps under test differ widely in filtrability. The German methods[22, 32] determine the clogging constant and generally are known to give values which agree with those by other methods only in case of viscose which are deficient in filtering properties. A method recently published by Vyas[33] gives a standardized laboratory procedure for making viscose solution and evaluating the filter value in terms of g. of viscose/sq.cm. filtering area till direct plugging takes place in case of badly filtering viscose solutions, and in the case of viscose solutions filtering rapidly, the plug point is estimated graphically.

To summarize, it can be said that constituents like pentosans, ash, low D.P. cellulose, etc. are undesirable in a viscose grade pulp; the pulp should be uniform and should have even polydispersity. Still it is difficult to say what exactly we want in a viscose grade pulp; hence, so long as a complete understanding of the physical and chemical characteristics of viscose grade pulps is not obtained, the industry would be using the empirical measurements of alpha-, beta- and gamma-cellulose, viscosity, polydispersity and filtrability of viscose pulps for their evaluation.

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Discussion

Shri M. P. Bhargava: In my opinion, studies of evaluation for viscose grade pulps should be restricted to those woods which are economically available in the country. We do not have enough supply of softwoods. Hardwoods of uniform quality and of the same species is also not available in enough quantity from one particular region. I would therefore suggest that such studies should be restricted to materials like bamboo which are economically and plentifully available.

Shri G. M. Vyas: Bamboo is similar to hardwoods in respect of chemical composition, and whatever I have said here for hardwood applies equally well to bamboo.

Dr. Lavji Thoria: In the last meeting of the Paper and Pulp Committee, it has been decided that a survey of existing raw materials for viscose grade pulp should be taken up. This, however, may take a long time. In the meantime, the industry carries out surveys and recently a decision has been taken to instal a plant to manufacture rayon grade pulp from bamboo, which is expected to start production in a few months.

Dr. P. K. Choudhury: When you say that alpha-cellulose is not uniform, do you refer to chain length or any other aspect ?

Shri G. M. Vyas: Besides the heterogeneity in chain length, there is also the non-uniformity due to association of different pentosans with cellulose.

Dr. A. B. Sen Gupta: Is there any cross linking between glucose and pentosans such as xylose?

Shri G. M. Vyas: I have no idea.

Dr. P. K. Choudhury: In your data, when you refer to 97 per cent alpha-cellulose, does this amount contain pentosans as well?

Shri G. M. Vyas: Yes.

Dr. Vikram A. Sarabhai & Dr. Lavji Thoria: There is no satisfactory information available for the differences in filtrability of different pulps. There is need for an intensive study of this problem.

Dr. P. K. Choudhury: Can poor filtrability be due to the presence of pentosans ?

Shri G. M. Vyas: Viscose solution does not follow Newtonian viscosity relations. For example, if the viscose solution is filtered through capillaries, a certain amount of coating of the capillary walls will occur. If the filtrate is filtered once again it will still give some more coating of the walls. Also the viscose solution has reversible aggregation–disaggregation behaviour. Many explanations for differences in filtrability can be given, but our present understanding of this problem is not complete.

Some Aspects of the Requirements of Dissolving Pulp for the Indian Rayon Industry

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The need for establishing a dissolving pulp mill in India for meeting the requirements of the rayon industry has been emphasized. Specifications for dissolving pulp, have been indicated and the possibilities of utilizing indigenous cellulosic materials, like bamboo and bagasse, for the manufacture of dissolving pulp have been discussed.

Dissolving pulp, a highly purified form of chemical pulp, is the chief raw material employed in the manufacture of rayon, cellulose acetate, cellophane, nitrocellulose, methyl cellulose, ethyl cellulose and other cellulose derivatives.

To meet the requirements of industry, which produces 47 tons of rayon per day, India at present imports dissolving pulp valued at Rs. 1.8 crores per annum. If we are able to utilize indigenous cellulosic raw materials and establish a dissolving pulp industry in India, we will be able to effect a saving in foreign exchange to the tune of Rs. 6.5 crores per annum.

Viscose Rayon Manufacture

In the manufacture of viscose rayon (Fig. 1 & Table 1 and Fig. 2), dissolving pulp, usually bleached sulphite pulp, is steeped in sodium hydroxide solution of 18 per cent strength at 20°C. for 1 hr. to form soda cellulose. The steeped pulp is then pressed to yield alkali cellulose which contains : cellulose, 30 ; sodium hydroxide, 15 ; and water 55 per cent. The pressed out alkali is generally reused after recovery. The pressed alkali cellulose is shredded at 23°C. for 1 hr. and aged in the presence of air at a temperature of 20°C. for *c.* 30 hr. Ageing is essentially a cellulose depolymerization step and is optimized to yield a product of the desired viscosity for later operations.

The aged alkali cellulose is then reacted with carbon disulphide at 28°C. for $2\frac{1}{2}$ hr. to form sodium cellulose xanthate. The xanthated mass

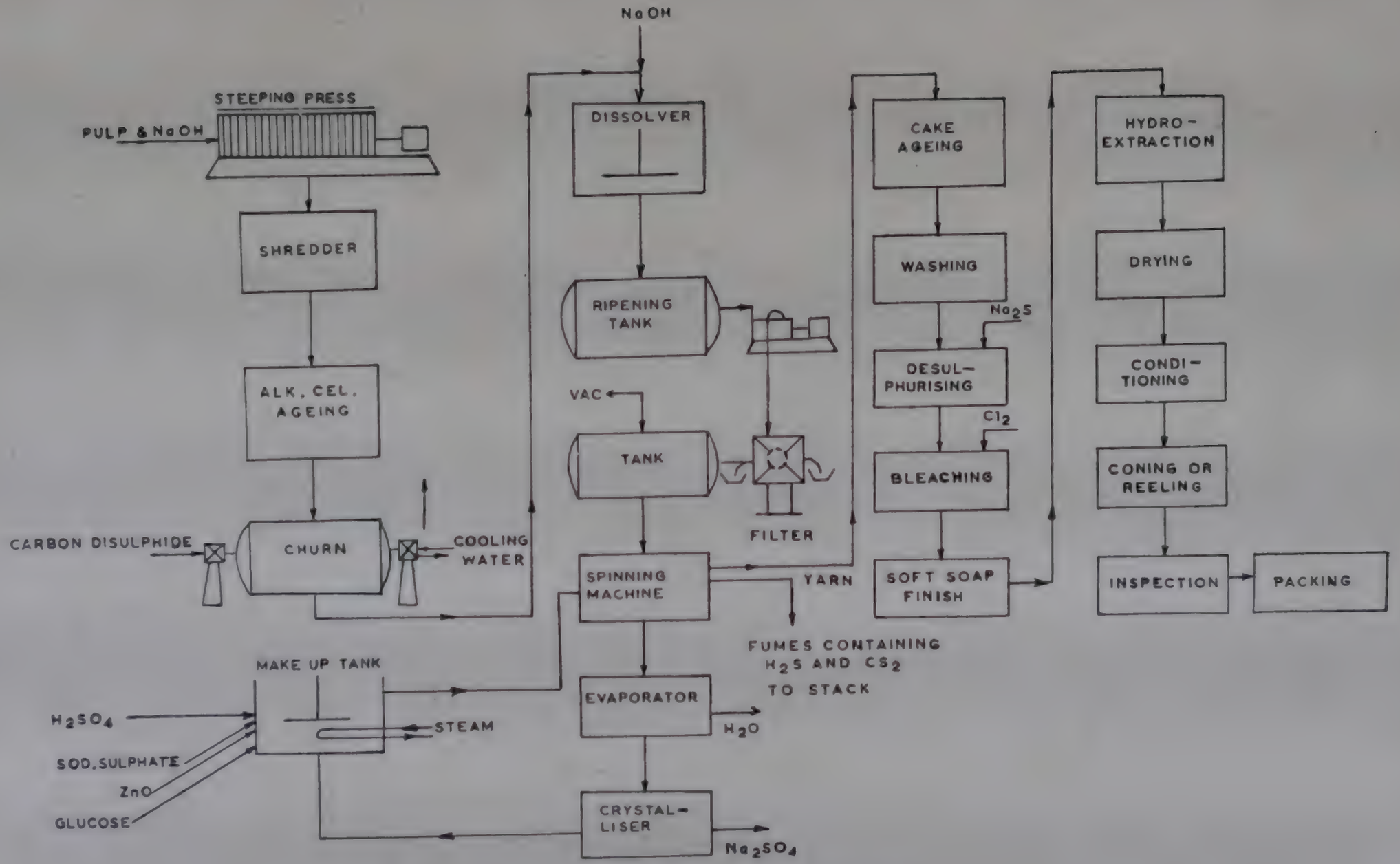

FIG. 1—MANUFACTURE OF VISCOSE RAYON—FLOWSHEET

TABLE 1—RAW MATERIALS AND UTILITIES REQUIRED PER LB. OF VISCOSE RAYON MANUFACTURED

Raw materials	*lb.*	Utilities	
Wood pulp	1.10–1.20	Steam	70 lb.
Caustic soda	1.00–1.10	Refrigeration	0.02 ton
Carbon bisulphide	0.35–0.40	Electricity	4.00 kw. hr.
Sulphuric acid	1.20–1.40	Water	200 gal.
ZnO	0.01	Direct labour	0.60 man hr.
Glucose	0.02		
Sodium sulphide	0.05		
Chlorine	0.01	Plant investment: Rs. 8 per lb. per year capacity	
Other materials	0.02		

is dissolved in dilute caustic solution at 18°C. in the course of $2\frac{1}{2}$ hr., to give colloidal 'viscose' containing: cellulose, 7.5; sodium hydroxide, 6.4; and total sulphur, 2.2 per cent. It is then filtered to remove unreacted cellulose fibres, foreign impurities and gels, deaerated under vacuum, and ripened at 20°C. for *c.* 40 hr. Cellulose xanthate partially de-esterifies during ripening, and many side reactions also occur.

Ripened viscose is pumped through spinnerettes into an acid spinning bath to give a continuous filament. During spinning, the excess of caustic is neutralized, xanthate is de-esterified and regenerated cellulose molecules are oriented by the spinning stretch. The spun yarn in the cake is then washed, desulphurized, bleached, finished, dried, conditioned and rewound in the form of cones or hanks.

Dissolving Pulp Specifications

In the selection of dissolving pulp, two major considerations are involved, namely: (i) commercial, e.g., price and availability, and (ii) technical, e.g., ease with which the pulp responds to rayon making and the effect of pulp constituents on the yield and quality of the final product. This paper deals mainly with the technical aspects of pulp selection.

Dissolving pulp is generally prepared from wood and as such, it contains wood constituents, the proportions of which depend upon the extent of pulping. The results of pulp analysis (Table 2) indicate that pulp contains alpha-, beta-, and gamma-cellulose extractibles, ash components and small proportions of other constituents.

Alpha-cellulose has been arbitrarily defined as the fraction which remains insoluble when pulp is treated with 17.5 per cent sodium hydroxide[3, 4], at 20°C. for 30 min. It corresponds to cellulose with a degree of polymerization (D.P.) exceeding 200[4]. Viscose rayon has a D.P. range of

TABLE 2--ANALYSES OF RAYON GRADE PULPS

Pulp	% Cellulose			Ether extract	Copper number	Ash %	Ash constituents (p.p.m.)			
	Alpha	Beta	Gamma				Iron	Calcium	Copper	Manganese
Kipawa Novocell (Canada)	90.70	2.54	6.52	0.23	..	0.11	7	219	0.2	..
Rayonier (U.S.A.)	91.80	1.67	6.21	0.18	..	0.13	5	189	0 3	..
Tongacell Rayon (U.S.A.)	93.10	1.60	4.74	0.16	..	0.06	10	189	0.3	0.3
Hawkesbury Novocell (Canada)	91.61	3.45	4.02	0.09	..	0.04	3	214	0.02	traces
Modosilk (Sweden)	94.17	3.02		0.15	..	0.03	9	104	4.3	0.4
Rauma (Finland)	89.03	10.07		0.38	..	0.10	21.6	129	3.2	4.3
Modosilk II (Sweden)	93.67	3.51		0.21	..	0.04	7.4	60	64	0.43
Billereud Church (Sweden)	94.05	4.14		0.51	..	0.06	..	..	..	..
Forss Silk (Sweden)	89.84	4.53		0.32	..	0.12	..	..	..	..
Uddeholm No. 31 (Sweden)	91.28	2.95	5.35	0.11	1.74	0.06	10	410	0.5	..
Uddeholm No. 32 (Sweden)	91.75	4.26	3.64	0.23	1.63	0.09	10	502	0.3	..
Bengtsfors Corona Super I (Sweden)	91.83	2.93	5.47	0.16	1.28	0.04	9	262	0.3	..
Modosilk No. 841 (Sweden)	90.31	3.23	5.70	0.11	1.57	0.03	6	113	0.3	..
Tamara Borregaard (Norway)	93.20	0.25	3.32	0.08	..	0.06	1	..	2.7	..

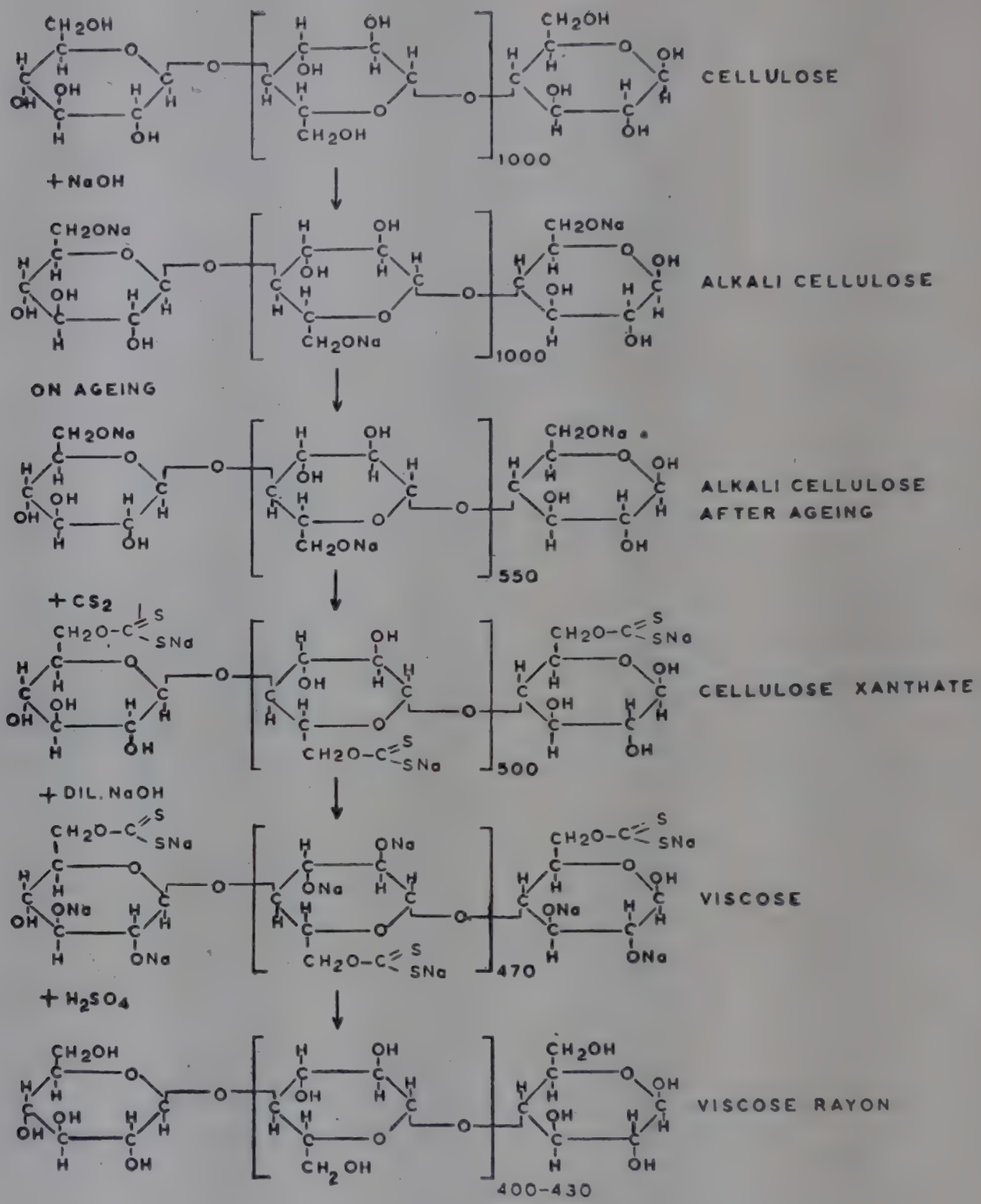

FIG. 2—PROBABLE CELLULOSE REACTIONS DURING MANUFACTURE OF VISCOSE RAYON

250 to 350 and the alpha-cellulose value gives a measure of the overall pulp yield and quality. Pulp consumers are interested in getting a pulp containing high alpha-cellulose. The determination of alpha-cellulose, however, provides no information on the polymolecularity of long chain molecules and this necessitates the measurement of D.P.

Hemicellulose is the term applied to polyoses, mainly xylans, arabinans, glucosans, galactans, mannans, etc., which are removable by cold or hot dilute alkali. As they are present in relatively small quantities in

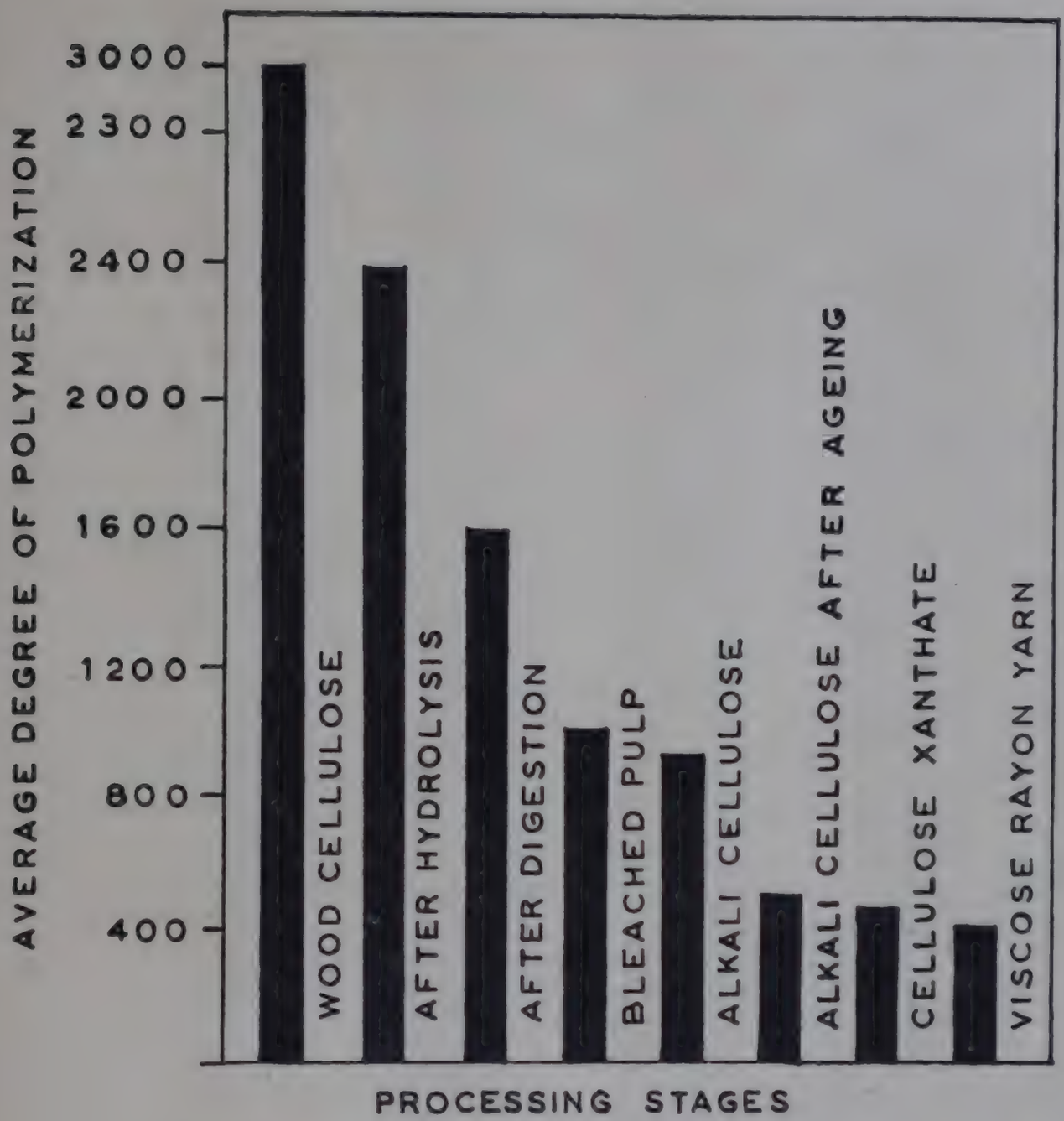

FIG. 3—PROBABLE CHANGES IN CELLULOSE D. P. DURING PROCESSING OF WOOD TO VISCOSE RAYON

dissolving pulp, rayon manufacturers evaluate hemicellulose in terms of Cross and Bevan's beta- and gamma-cellulose.

A certain amount of hemicellulose is necessary in paper pulp in order to impart a high degree of hydration, but for dissolving pulp, except for that required for sheet formation and its swelling, hemicellulose is usually an undesirable constituent. Cellulose molecules of less than 200 D.P. are usually incapable of producing a coherent fibre[7]. It is still uncertain whether the chemical configuration of hemicellulose influences pulp quality; the degree of polymerization and its physical state are far more important than chemical constitution.

Beta-cellulose is that fraction which gets precipitated when soluble pulp extractibles, obtained by treating pulp with 17.5 per cent sodium hydroxide at 20°C. for 30 min., are neutralized[4]. This fraction includes polyoses[4, 6] with D.P. ranging from 10 to 150.

Gamma-cellulose is that fraction which remains in solution[4] when the soluble extractibles obtained by treating pulp with 17.5 per cent sodium hydroxide at 20°C. for 30 min. are neutralized[4]. This fraction includes polyoses[6] with D.P. up to 10.

Low molecular fractions of cellulose that remain unextracted during steeping undergo xanthation and appear in the yarn. They do not contribute to yarn tenacity and they, therefore, act as diluents or fillers. Moreover, the solubility of cellulose xanthate is influenced by the chain length of cellulose; the smaller the chain length, the greater the solubility of the xanthate found. Soluble xanthates hinder the effects of spinning stretch[8]. It is desirable, therefore, to keep the concentration of low molecular fractions to a minimum.

Degree of polymerization—The effect of chain length distribution on the properties of rayon has been extensively studied[9, 10]. The changes in the D.P. of celloluse during viscose rayon manufacture are given in Fig. 3. A rayon pulp of good quality should be as uniform as possible with respect to molecular size, and the purpose of ageing in viscose manufacture is to make the chains uniform with respect to D.P.

Cellulose degradation to a D.P. of *c.* 500, as brought about by the oxidation of alkali cellulose, removes the differences in molecular weight distribution in pulps. It appears, therefore, that molecular weight distribution is not an important characteristic of viscose pulps which are subjected to alkaline ageing[11].

The yarn tenacity increases with the increase in D.P. up to 350–400, after which the relationship is asymptotic. Published work[9] in this field indicates the desirability of keeping the D.P. of finished yarn in the range of 375–450 (Fig. 4).

Copper number—The reducing power of cellulose is usually expressed as copper number, which represents the copper in Fehling's solution reduced by 100 g. of cellulose. The copper number of cotton cellulose[12] ranges from 0.05–0.08; higher copper numbers indicate degradation. Bleached sulphite wood pulps have a copper number of 1.5–2.5 and as it provides chiefly a measure[13] of hydrocellulose and oxycellulose in the pulp and gives no additional information to that given by alkali solubility and viscosity tests, the copper number is seldom determined.

The non-cellulosic constituents of pulp have a pronounced effect on processibility. They should be as low as possible without affecting the uniformity of the pulp.

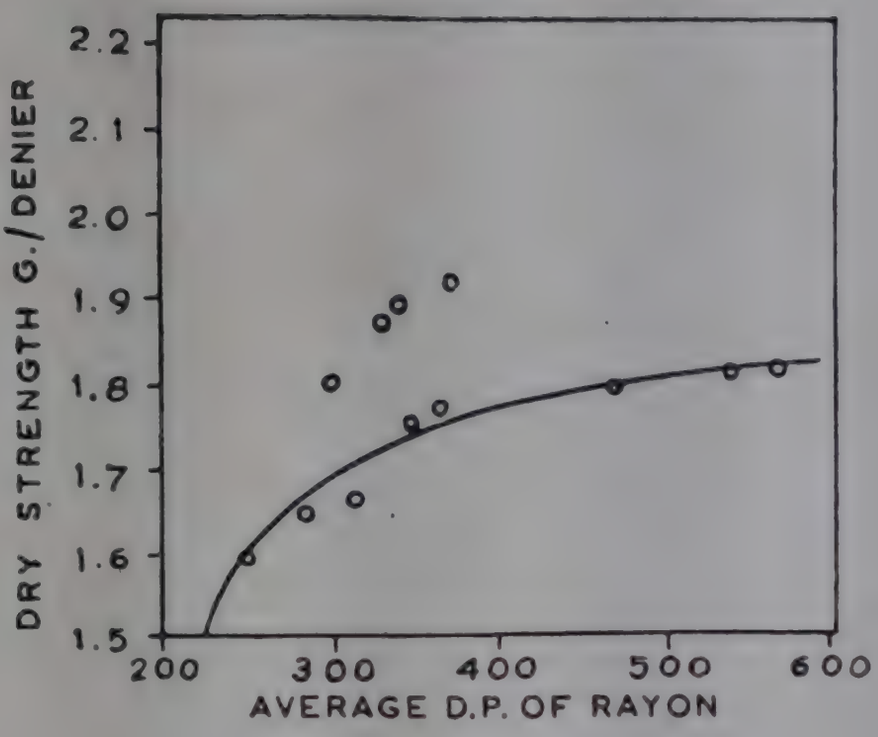

FIG. 4—TENACITY VS. D. P. OF RAYON

Ash constituents—Alkaline earths, such as calcium and magnesium, hinder pulp reactivity and result in poor viscose filtration. High percentage of silica also has a similar effect. Calcium is detrimental also because it tends to cause incrustations around spinnerette holes[14].

The rate of alkali cellulose ageing is distinctly influenced by the presence of certain metals, such as iron, nickel, cobalt, cerium, vanadium, chromium and manganese[15], which catalyse the ageing process. Nickel has the lowest, and chromium and manganese the highest catalytic effect.

As little as 0.1 per cent iron in wood pulp reduces the ageing time of alkali cellulose to one-fourth the normal ageing time. Even smaller concentrations of iron (0.0018–0.015%) has an appreciable effect on cellulose depolymerization. The presence of copper in small amounts has no effect.

The concentration of lignin, a polymer of phenyl propane groups, should be as low as possible[16] in pulp. Its presence interferes with pulp reactivity.

Ether extractibles—Pulp constituents soluble in organic solvents, like ethyl ether, are fats, fatty acids, resins, waxes and non-volatile hydrocarbons. In small quantities, they act as wetting and emulsifying agents and are, therefore, useful.

Pulp processibility is usually measured by converting the pulp to xanthate and determining the ease with which the xanthate dissolves in caustic as measured by the filtration characteristics of viscose. Filtration is influenced by the processing conditions adopted for viscose manufacture, filter area, filter media and the pressure drop maintained during filtration. The filtration test can be conveniently used to predict pulp processibility

by comparing the plot of $d\ v/d\theta$ vs. $1/v$ (v=volume of viscose filtered, θ =time in min.) for a pressure drop of 20 lb./sq. in. using the same filter media and viscose processing conditions as that used in commercial manufacture. A laboratory scale set-up with a filter area of 12 sq.cm. will suffice for the test.

Pulp uniformity—Dissolving pulp should be uniform in quality throughout the consignment and also from consignment to consignment. Slight differences in viscosity, xanthate solubility, ash constituents, etc., can have pronounced effect on processing conditions. For stable operation, it is essential that the variations should be very small.

Sutermeister[13] recommends that the viscosity may be considered uniform if viscose made from ten 60 lb. samples of successive lots of pulp does not vary by more than 6 per cent from the average. Pulp uniformity can also be judged by the alpha-cellulose content of pulp which should not vary by more than ± 1 per cent from the average.

The pulp should also show uniformly high solubility as gauged by the filtration characteristics of viscose made from successive lots.

Geometry of pulp sheets—Steeping is an important processing requirement as far as sheet formation is concerned. A pulp which does not steep well is likely to cause difficulty in the subsequent operations of ageing, xanthation, filtration and spinning. Even under the best commercial conditions, the geometry of books, that is, sheet size, spacing, etc., results in a gradient in alkali content from outside sheets to the central sheet. To avoid this, the pulp sheet should be designed to absorb alkali evenly. The absorption properties of the fibre mass must be balanced against the physical design of pulp sheet. With a correct match between absorption rate and rate of caustic rise due to capillary action, the steeped sheet should neither float nor slump in the press, and it should be free from areas of incomplete penetration. The importance of pulp qualities which affect steeping cannot be over-emphasized, because there are no known ways of adjusting the subsequent processing stages to compensate for the damage suffered from non-uniform steeping.

The effect of different constituents of pulp on the manufacture of rayon have been studied by a number of investigators in Europe, U.S.A., Canada and Japan. Based on their results and our own experience in this field, we have arrived at the following specifications for dissolving pulp (Table 3).

As it is not possible to get an exact idea of the quality of rayon which is produced from given pulp specifications, complete evaluation of pulp by pilot plant tests is necessary.

Indigenous Raw Materials

Dissolving pulp is manufactured in U.S.A., Canada, Sweden and Norway mainly from softwoods, like spruce, hemlock, fir, etc., by the sulphite

TABLE 3—SPECIFICATIONS FOR DISSOLVING PULP

(percentage on dry basis)

α-cellulose	Greater than	90
β-cellulose	Less than	4
γ-cellulose	Less than	5
Extractibles	Less than	0.5
Ash	Less than	0.1
Brightness (Higgins)	Greater than	85
Viscosity (Tappi)	Around	30 cP.
Copper number	Less than	2
Ash Constituents:		
Iron	Less than	0.0010
Copper	Less than	0.0005
Calcium	Less than	0.03
Magnesium	Less than	0.005
Silica	Less than	0.01
Manganese	Less than	0.0001

process. Up to 1940, only softwoods were being employed ; more recently, dissolving pulp is produced by the modified kraft process from woods such as beech and poplar.

As far as the availability of cellulosic raw materials in India is concerned, we are faced with the following problems : scarcity of softwoods ; availability of suitable wood species ; utilization of agricultural waste ; sulphur shortage and utilization of sodium sulphate obtained as a by-product in rayon manufacture.

A few coniferous species are available in Himalayan terrains, but excessive transport costs limits their commercial exploitability. There are other indigenous raw materials, like bamboo and bagasse, which deserve consideration for dissolving pulp manufacture. Table 4 gives a comparison of indigenous cellulosic raw materials with those used in foreign countries.

Bamboo—An interesting point about bamboo is that once cut, it grows again rapidly. Certain species of bamboo, unlike pulpwood, have the advantage of being harvestable at relatively short intervals of 6 years. On a conservative estimate, a bamboo forest, 16 sq. miles in area, would be sufficient to supply raw material for a 50-ton pulp mill indefinitely[17].

The striking difference between bamboo *(Dendrocalamus strictus* and *Bambusa arundinacea)* pulp and hardwood is the relatively high ash content of the former. Attempts are being made to eliminate the ash constituents by suitable processing. Raitt's kraft process, preceded by hydrolysis and followed by the conventional four-stage bleaching, seems to be suitable for pulping bamboo (Fig. 5 and Table 5).

Bagasse is one of the largest potential cellulosic raw materials available for utilization by the Indian pulp and paper industry. About 2.4 million tons of bagasse are annually available for sugar mills. It contains 45 to

TABLE 4—RAW MATERIALS FOR DISSOLVING PULP MANUFACTURE

Raw material	Proximate analysis, %					Pulping process	Yield
	Ash	Cellulose	α-cellulose	Pentoses	Lignin		%
Western countries :							
SOFTWOODS							
Spruce	0.31	59.8	44.3	10.4	29.2	Sulphite process	46.5 (Unbleached)
Hemlock (Eastern)	..	53.0	37.8	9.5	34.5		
Hemlock (Western)	..	59.3	42.3	9.6	30.5		
Fir (Lowland white)	..	63.0	45.9	8.9	27.0		
Fir (Dougas)	0.38	59.6	42.6	10.0	30.0		
Pine (Jack)	..	58.3	42.8	14.0	29.9		
Pine (Longleaf)	0.37	60.3	44.2	12.7	31.8		
Cedar	..	56.4	36.8	12.3	34.2		
HARDWOODS							
Beech	0.96	51.9		24.3	22.7	Sulphite process	34.6 (Bleached)
Poplar	1.21	56.0		24.3		Nitric acid pulping	
					22.7	Modified sulphate process	37.4 (Bleached)
GRASSES							
Arundo donax						Bisulphite process	
Straw						Modified kraft process	
Indigenous* :							
Bambusa arundinacea	2.56	49.2		24.6	15.2	Fractional soda process	36.9 (Bleached)
						Fractional sulphate process	38.9 (Bleached)
Dendrocalamus strictus	2.45	62.9		19.5	24.5	Fractional sulphate process	40 (Bleached)
Bagasse	1.9			26.8	21.1	Modified sulphate process	51 (Unbleached)
Blue gum (Eucalyptus)	0.25	60.9		15.5	20.3	Conventional sulphate process	56 (Unbleached)
Sabai grass	4.16	52.3		27.2	16.1	Conventional soda process	

* Values taken from published work

TABLE 5—RAW MATERIALS AND UTILITIES REQUIRED PER TON OF DISSOLVING PULP

Raw materials	*Tons*	Utilities	
Wood	3.25	Water	50,000 U.S.G.
Sulphuric acid (100%)	0.10	Steam	16,663 lb.
Saltcake ($Na_2SO_4.10H_2O$)	0.153	Power	400 kw. hr.
Limestone	0.235	Direct labour	35 man hr.
Chlorine gas	0.029		
Sodium hypochloride	0.0189		
Chlorine dioxide	0.02	Plant investment : Rs. 2,500 per ton per year capacity	

50 per cent of water and about 30 per cent pith. Methods have recently been devised for separating pith for the fibre. The average fibre length is 1.5–2.0 mm.

At present, most of the bagasse is used as fuel in sugar mills. If all the bagasse is utilized for pulping, the annual production of pulp and paper can be increased by 1 million tons. The pulping procedure employed for bamboo, or the Pomilio process, can be employed for the preparation of dissolving pulp from bagasse.

Economics of Manufacture

A preliminary study for determining the economic feasibility of establishing a dissolving pulp mill in India has been made (see Fig. 6). The following points have emerged from the study :

(i) The break-even capacity of a dissolving pulp mill is around 9,000 tons per year, i.e., 24 tons per day ; (ii) the approximate cost for a 50-ton per day capacity dissolving pulp mill will be Rs. 2,15,00,000 ; and (iii) the large bulk of variable cost is the cost of raw materials (*c.* 52% of the total cost of production). Maintenance and utility requirements form the next largest operational cost. This suggests that a detailed study of raw material consumption would help to reduce the cost of production.

The study suggests that rayon manufacturers, with the co-operation of pulp and paper manufacturers and the Government of India, should make serious attempts to set up a dissolving grade pulp mill with a minimum capacity of 50 tons/day. The setting up of a second unit may be taken up at the end of the second Five-Year Plan period.

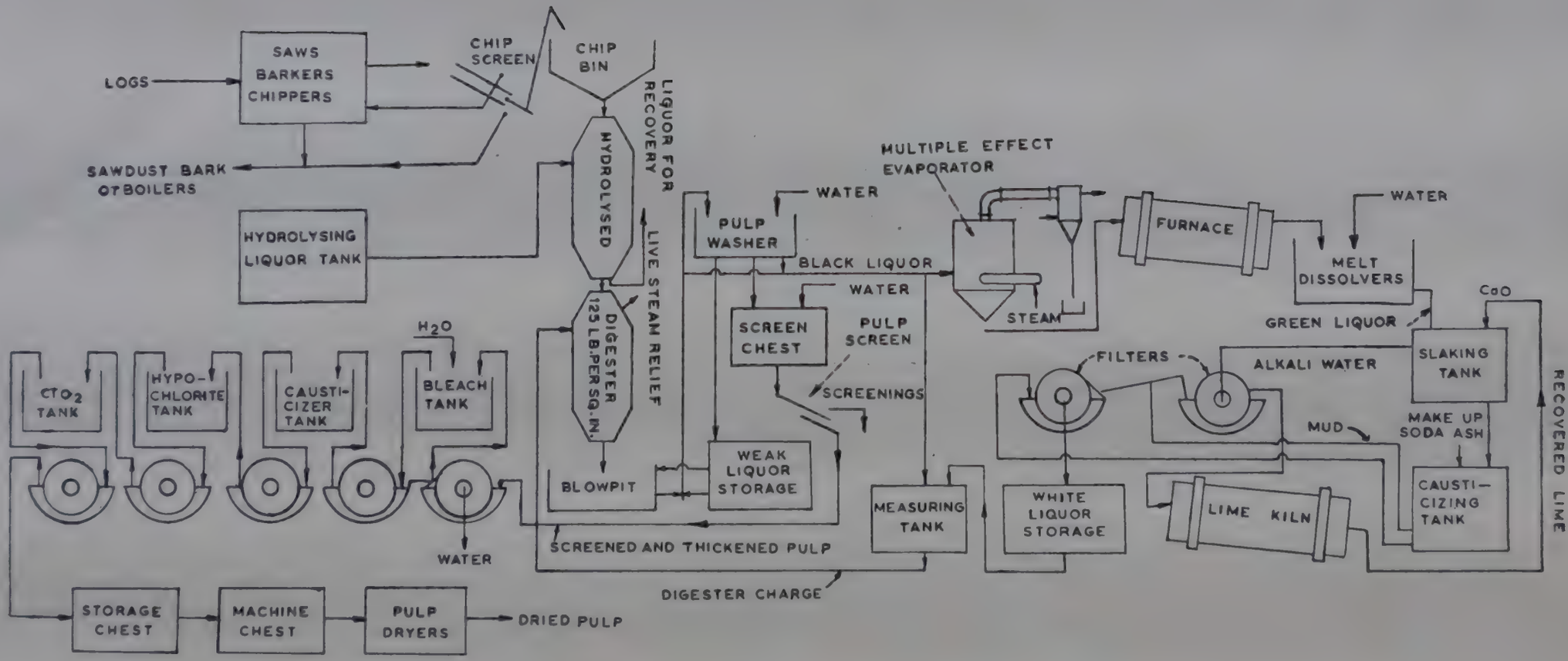

FIG. 5—MODIFIED KRAFT PROCESS

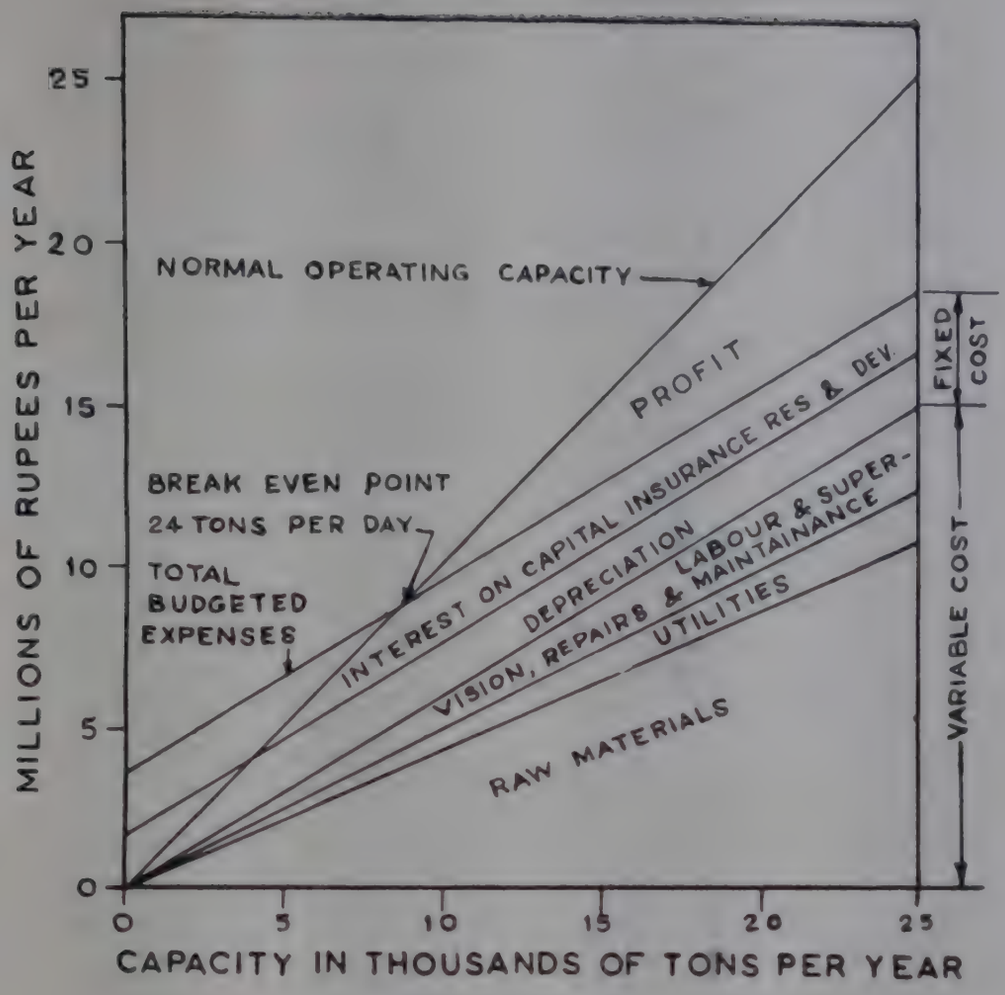

FIG. 6—BREAK-EVEN CHART

The National Rayon Corporation has undertaken an extensive study of raw materials and pulping techniques. The selection of a pulping process and the optimization of pulping variables for each raw material constitute the main objectives of the laboratory work. Pilot scale studies will be conducted to further pin down the variables for detailed study of process economics.

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Anti-crease and Anti-shrink Finishes for Viscose Rayons

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The results of work carried out at the Shri Ram Institute on the treatment of viscose rayons with acidic formaldehyde solution containing hydrophilic agents, and with Srifirset (a carbohydrate derivative of urea) have been presented. The Srifirset process has been briefly described and the properties of treated fabrics have been given.

Viscose rayon, a regenerated cellulose fibre, is significantly different from the natural cellulose fibre, cotton. The former has a low degree of polymerization (D.P., 250–600), compared to cotton (D.P., 3,000 and above); it is highly amorphous, the crystallinity being 25–40 per cent as compared to 70–80 in cotton. The characters which viscose rayon possesses owing to these properties are: (i) greater susceptibility to dimensional changes when washed; (ii) low wet strength; and (iii) low tensile strength per unit cross-section compared to cotton.

Apart from molecular configuration, the strains introduced during spinning and weaving, and the strain introduced in rayon fabric during the various stages of dyeing and finishing, have a marked effect on the dimensional behaviour of the fabric. The combined effect leads to a shrinkage of 20–25 per cent in georgettes and a shrinkage of 7-15 per cent in satins, crepes, staple fibre fabrics, etc.

Attempts have been made from time to time to improve the properties of viscose rayon by suitable chemical modification. The earliest attempt by Eschalier is noteworthy. The process proposed by him involved the use of formaldehyde in the presence of acidic catalysts, and it was claimed that shrink resistance and tensile properties of rayon improved as a result of the treatment. The process did not, however, attain commercial success. Interest in the aldehyde treatment of textiles was revived after the end of the first World War. In 1928, Marsh *et al.* (*Tootal Broadhirst & Lea Co.*) made a notable contribution when they introduced the urea-formaldehyde anti-crease process. Since then, a number of firms in U.S.A., U.K., Germany, Holland, Japan, etc. have made

notable contributions in this field. The main lines of work are: (i) treatment with synthetic resin pre-condensates formed from urea-melamine or their derivatives and formaldehyde; (ii) treatment with aldehydes alone, such as formaldehyde, glyoxal, etc., and (iii) treatment with other cross bonding agents, such as vinyl sulphone, epichlorhydrin, potassium disulphate, ethylamine, etc.

Later attempts were in the direction of modifying either the properties of resins or those of cross linking agents in such a manner that there is an improvement in one or more of the following aspects: (i) reduction in brittleness resulting in softer handle; (ii) reduction in chlorine retention resulting in better bleachability; (iii) improvement in wet tensile and wear values; and (iv) improvement in process details, such as type of catalysts, protective agents, and temperature or manner of curing.

India manufactures *c.* 500 million yards of rayon cloth. A large part of it is processed neither for anti-creasing nor for anti-shrinking (stabilizing). There is an increasing demand for Indian rayon fabrics, particularly in middle and south east Asia. Processing of fabrics for anti-creasing and anti-shrinking will improve the quality of products and stimulate foreign demand.

The Shri Ram Institute took up studies on anti-crease and anti-shrink finishes in 1953. Available techniques were first examined, and later, a new compound, designated Srifirset, which could be used for improving the anti-crease and anti-shrink properties of rayon fabrics was discovered.

Resin finishes and formaldehyde treatment

Methods for the preparation of urea-formaldehyde pre-condensate and for treating rayon goods were worked out. The stability of the treating solution was studied at different temperatures and the 'know-how' of the process was developed with the object of rendering help to those interested in the process.

The process which uses resins and the process which uses formaldehyde alone, involve three steps: (i) Padding with treating solution, (ii) drying, and (iii) curing at high temperature.

Attempts were made to simplify the process to eliminate the need for curing. On analysing the normal formalizing process, it was found that free water present in the treating solution made high temperature curing imperative. A process was evolved in which the free water was bound by the addition of hydrophilic compounds, such as calcium chloride, magnesium chloride and aluminium sulphate. The new process consists in simply treating rayon textiles with a solution containing formaldehyde, acid catalyst and a hydrophilic agent, say calcium chloride, for a certain duration at room temperature, washing and then drying. No baking is necessary. All forms of textile material, viz., fibres, yarns

TABLE 1—EFFECT OF VARYING THE DURATION OF IMPREGNATION ON YARN

(Treating bath: $CaCl_2$, 30; HCHO, 10; HCl, 2 per cent; temp., 60°C.)

Duration of impregnation *min.*	Shrinkage %	Loss in tensile strength %	Decrease in elongation %
3	1.6	8.0	36.2
5	1.0	13.0	37.2
30	nil	15.0	40.4
Untreated	9.8	0	0

TABLE 2—EFFECT OF VARYING THE BATH ACID CONCENTRATION ON YARN

(Treating bath: $CaCl_2$, 30; and HCHO, 10 per cent; temp., 22°C.)

Acid concentration %	Shrinkage %	Loss in tensile strength %	0
			38.2
1	1.4	7.4	26.5
2	0.6	10.4	% elongation
Untreated	10.6	0	Decrease in

TABLE 3—EFFECT OF INCREASING THE DURATION OF IMPREGNATION ON FABRICS

(Treating bath: $CaCl_2$, 30; HCHO, 10; and HCl, 0.5 per cent; temp., 30°C.)

Duration of impregnation *hr.*	Shrinkage, %		Loss in tensile strength (warp) %	Decrease in elongation %
	Warp	Weft		
4	2.7	4.3	29.5	20.9
16	0.3	0.7	32.9	37.3
24	..	0.7	42.5	42.4
Untreated	10	7	0	0

and fabrics, can be treated, and treated fabrics possess better draping qualities and crease recovery; they are also shrink-proof.

As the process appeared attractive a detailed study was undertaken. The effect of different variables, such as duration of impregnation and concentration of acid in the treating bath, were studied. The results are given in Tables 1 and 2.

By increasing the duration of impregnation or the concentration of acid in the treating bath, the shrinkage is reduced and the loss in tensile

TABLE 4—EFFECT OF VARIATION IN SRIFIRSET : FORMALDEHYDE RATIO ON YARN

(Catalyst, NH_4Cl; drying temp., 120°C.)

SRIFIRSET: FORMALDEHYDE RATIO	WEIGHT INCREASE %	CREASE RECOVERY, %		LOSS IN TENSILE STRENGTH %
		Weft	Warp	
1:2	3.02	..	..	..
1:5	6.96	47	43	5.39
1:7	10.06	65	57	2.50
1:10	12.25	71	60	25.00
Untreated	0	37.7	31.5	0

strength is increased. The result was confirmed by experiments carried out with woven fabric in place of yarn (Table 3). As the loss in tensile strength is high, the process has no practical utility.

SRIFIRSET PROCESS

The normal urea-formaldehyde process suffers from the following disadvantages : (i) unstability of treating bath, (ii) many steps, such as padding, drying and curing, involved in the treatment, and (iii) embrittlement of treated fabrics. Attempts made to overcome these defects, resulted in the discovery of a compound, Srifirset (a carbohydrate derivative of urea) and the development of a process for utilizing Srifirset with formaldehyde.

Development

The development work involved a detailed study of Srifirset : formaldehyde ratio in the bath, Srifirset concentration, *p*H of the bath, temperature of treatment and duration of drying. The results are summarized in Tables 4–9.

It has been observed that when the *p*H of the treating bath is lowered, the shrinkage is reduced. The combined Srifirset increases as the temperature and duration of drying increases ; but long exposure at high temperatures results in yllowing with loss of tensile strength. The higher the temperature of drying, the lower is the shrinkage. Among the catalysts tried, a mixture of sulphuric acid and aluminium sulphate appears to be the best from the point of view of dimensional stability and minimum loss in tensile strength ; ammonium chloride is the best from the point of view of anti-crease properties. It will be seen from the results set out in Tables 4–9 that the optimum conditions for the treatment are approximately as follows : Srifirset–formaldehyde ratio, 1:7; Srifirset concn., 12 per cent for crepes and 8 per cent for georgettes ; *p*H, 2.5 ; drying temp., 90–140°C. ; and duration of drying, 1–10 min.

TABLE 5—EFFECT OF VARYING SRIFIRSET CONCENTRATION ON CLOTH

(Srifirset: HCHO, 1:7; pH, 2.5; drying temp., 120°C., duration, 5 min.)

Fabric	Srifirset concentration %	Weight increase %	Shrinkage, %		Loss*/gain in tensile strength, %			
					Dry		Wet	
			Weft	Warp	Warp	Weft	Warp	Weft
Crepe	8.0	..	2.5	1.6	—8.3	18.0	33.0	15.0
Crepe	12.0	..	..	1.0	—12.0	nil	25.0	8.0
Crepe (blank)†	20.0	..	2.1 (10.0)	1.0 (11.3)	—19.0	—37.6	..	—25.0
Georgette	8.0	3.6	0.8	6.0	—16.0	33.0	63	30.0
Georgette (blank)†	12.0 (12.0)	5.8	0.8 (17.3)	2.5 (24.8)	—38.0	—10.0	18	—6.0

*Loss indicated by — sign

† Figures in bracket give shrinkage of untreated cloth

TABLE 6—EFFECT OF *p*H OF BATH ON FABRIC

(Srifirset: HCHO, 1:7; catalyst, $Al_2(SO_4)_3$, H_2SO_4; drying temp., 100°C.; duration of drying, 1 min.)

Fabric	*p*H of soln.	Shrinkage, %		Loss in tensile strength, %	
		Warp	Weft	Warp	Weft
Treated	2.45	5.0	10.4	..	..
Treated	2.00	4.0	6.0	..	..
Treated	1.50	0.3	3.8	37.0	30.0
Stable fibre fabric (blank)	..	6.3	11.0	..	..

TABLE 7—EFFECT OF TEMPERATURE AND DURATION OF DRYING ON COMBINED SRIFIRSET*

(Srifirset: HCHO, 1:7; pH 2.5; catalyst, NH_4Cl)

Drying temp. °C.	Duration of drying *min.*	Combined srifirset*	Remarks
90	5	2.66	..
120	5	8.94	..
140	5	10.94	Yellowed
90	10	9.57	..
120	10	15.72	Yellowed

* Combined Sriferset refers to percentage increase in weight of the treated fabric, which corresponds to the amount of Sriferset and formaldehyde combined with the fabric

TABLE 8—EFFECT OF DRYING TEMPERATURE ON CLOTH

(Srifirset: HCHO, 1:7; pH, 2.5; catalyst, $Al_2(SO_4)_3$, H_2SO_4; duration of drying, 5 min.)

Cloth	Drying temp. °C.	Warp shrinkage %
Treated	100	9.0
Treated	120	2.3
Blank	..	11.6

Outline of the process

The textile fabric from the loom is desized, scoured, dyed or printed as required and dried to the dimensions at which the fabric is to be stabilized. It is then dipped in a solution of Srifirset, squeezed to 100 per cent squeeze and directly dried at 90–140°C. for periods ranging from 10 to 1

TABLE 9—EFFECT OF DIFFERENT CATALYSTS ON FABRIC

(Srifirset: HCHO, 1:7; drying temp., 120°C.; duration of drying, 5 min.)

Catalyst	*p*H	Increase in weight	Shrinkage, %		Loss in dry tensile strength	Crease recovery, %	
		%	Warp	Weft	%	Warp	Weft
H_3PO_4	2.59	4.63	..	..	7.4	53	41
H_2SO_4	2.52	2.89	7.0	6.0	7.4	48	43
HNO_3	2.45	7.13	3.2	2.8	22.7	48	46
NH_4Cl	2.84	10.55	..	..	44.5	69	62
$Al(NO_3)_3$. HNO_3	2.50	9.58	0.6	0.4	56.0	67	52
$Al_2(SO_4)_3$, H_2SO_4	2.57	7.15	0.4	0.0	13.3	52	42
Untreated cloth	..	..	10.0	11.0	..	42	37

TABLE 10—PROPERTIES OF SRIFIRSET FABRICS

(Figures in bracket give shrinkage of untreated cloth)

Fabric	Shrinkage, %		Loss*/gain in tensile strength, %				Improvement in impact tear value, %			
			Dry		Wet		Dry		Wet	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
Staple fibre fabric	2.5 (10.0)	2.6 (11.0)	12.3	9.0	39.0	48.0	1.0	5.9	15.5	15.0
Crepe	2.5 (10.0)	1.6 (11.3)	–8.3	18.2	34.1	15.0	..	..	..	..
Satin	1.9 (9.0)	1.8† (–2.0)	–8.2	34.5	51.6	57.2	..	..	..	..
Georgette	2.5 (17.1)	3.0 (24.8)	–15.6	–23.0	23.6	–7.0	..	..	..	..

* Loss indicated by —sign

† Elongation increase, c. 6%

TABLE 11—CHLORINE RETENTION UNDER DIFFERENT TREATMENTS

Fabric	Treatment	Chlorine retained %
Staple fibre	Untreated	0.041
Stable fibre	U.F.	1.807
Stable fibre	Tootal, U.F.	1.991
Binny's Hanava	U.F.	1.661
Staple fibre	Srifirset	0.609

U.F. = Urea-formaldehyde

minutes depending on the temperature. Treated and dried fabric is then washed in alkaline soap and dried to the desired dimensions.

Properties of treated fabrics

Treated fabrics are dimensionally stable and do not shrink or elongate on wetting or washing. They suffer a dry tensile loss of 0–15 per cent depending upon the nature of the fabric and the extent of dimensional stability obtained; but the wet tensile strength increases by 20–40 per cent. The fabrics have a better drape and garments made of them retain shape better. They are softer and fuller, and possess improved crease-resistance, though not to the same extent as urea-formaldehyde treated fabrics. They absorb 75 per cent less chlorine than fabrics treated with urea-formaldehyde resin and in this respect, they are superior to the latter. They have improved wear properties (Tables 10 and 11).

TABLE 12—PROPERTIES OF SRIFIRSET FABRICS

(Trials in Sadhana Textile Mills, *Bombay)*

Cloth	*p*H	Time *sec.*	Temp. °C.	Shrinkage, %		Loss*/gain in tensile strength, %			
						Dry		Wet	
				Warp	Weft	Warp	Weft	Warp	Weft
Crepe (blank)	..	..	..	(12.0)†	(11.7)	..	..	..	..
Crepe	2.5	120	130	3.8	4.0	–1.0	–9.5	81.0	9.2
Crepe	2.5	240	130	2.7	1.6	–8.8	–14.6	52.0	3.7
Crepe	2.0	120	130	3.2	1.0	..	..	..	..
Crepe	1.6	50	130	0.4	1.9	–28.0	–30.0	–4.0	4.0
Georgette (blank)	..	..	..	(14)	(12.8)	..	..	..	..
Georgette	1.8	50	125	2.8	0.9	–30.0	–46.0	–10.0	–26.0
Satin (blank)	..	..	..	(7.2)	(5.5)	..	..	..	..
Satin	2.5	50	120	8.0	6.2	..	..	..	..
Satin	2.5	150	120	2.0	0.9	..	..	..	..

* Loss in tensile is denoted by —sign

† Figures in brackets give shrinkage of untreated cloth

Equipment

The drying operation is critical and the efficiency of the process depends on the control of temperature, humidity and air velocity inside the drying chamber and the time of drying. Generally, any factory which possesses a good padding mangle and a drying chamber provided with air circulation, can make use of the process. Tenters in particular are advantageous for this process, because there can be as much as 8–10 per cent gain in cloth dimensions if the treatment is done under stretched conditions. However, the attainment of required processing conditions in a given tenter has to be carefully worked out by preliminary trials.

During the processing treatment, there is the odour of formaldehyde in and around the working place, but this can be avoided by the provision of hoods and suction fans on padding mangles and tenters.

Large scale trials

Factory trials of the Srifirset process have been carried out at the *Sadhana Textile Mills,* Bombay using different types of fabrics, viz., crepes, satin, georgettes, etc.

By employing a treating bath of *p*H 2.5, a shrink-proof cloth was obtained when the duration of treatment was 3–4 min. A longer treatment was not possible with the tenter available in the mills. A fully shrink-proof cloth was obtained when the *p*H was 1.6, but at this *p*H, there was loss in dry tensile strength and no gain in wet tensile strength. This difficulty could be overcome by using suitable drying machinery. The properties of Srifirset fabrics produced in experimental trials in the *Sadhana Textile Mills* are given in Table 12.

Some advantages

(i) Unlike the urea-formaldehyde pre-condensate, which cannot be stored for more than 4–6 hr., Srifirset solutions are stable.

(ii) Urea-formaldehyde resin has a tendency to migrate to the surface of the fibre during drying, thereby producing brittleness and harshness. Srifirset shows no such tendency and the fabric remains soft.

(iii) Urea-formaldehyde resin being unstable cannot be made available in ready made form; Srifirset can be supplied ready made.

(iv) Most of the other processes envisage a three-stage treatment, namely, padding, drying and heat treatment. In the Srifirset process, the treatment involves only two stages : padding and drying.

Cost of treatment

The cost of the treatment depends to a large extent on the type of fabric treated. Roughly it ranges from 2–3 annas per lb. of treated cloth for lightly woven fabrics and 5–8 annas per lb. for thickly woven fabrics.

Acknowledgment

Thanks are due to the Textile Division of the Institute for technical assistance, to the Cellulose Research Committee, CSIR, for providing an opportunity to present the paper, and to the Director, Shri Ram Institute for Industrial Research, for providing facilities for laboratory work.

Discussion

Dr. P. C. Mehta: There is a well-known commercial process involving the use of starch with urea-formaldehyde. How is your process different from this and what is the main advantage of your process ?

Shri K. Manivannan: We have reduced the curing time by using highly acidic catalysts.

Dr. V. B. Chipalkatti: Starch urea-formaldehyde finishes give a harsh feel and are not as wash-fast as those obtained by our process. Our process imparts a soft and supple feel to fabrics.

Shri S. S. Trivedi: Which carbon atom of glucose combines with the N of urea in your resin ?

Dr. V. B. Chipalkatti: We have not tried to follow the reaction mechanism, but I can suggest two possibilities: the reaction may be either at the first carbon atom or at the second or third carbon atom. We do know that a definite compound with a sharp melting point is formed as a result of the reaction.

Shri R. J. Chikte: You have used calcium chloride in some of your experiments. What is the purpose of adding calcium chloride ?

Dr. V. B. Chipalkatti: In the reaction of cross linking agents with cellulose, water is liberated. The addition of a hygroscopic material, such as calcium chloride, is expected to favour the cross linking reaction, and this has been proved by the data presented.

Dr. Vikram A. Sarabhai: In your data, you have shown values of tensile strength such as 3.2 and 2.8. Have you tested these results statistically for significance of difference?

Dr. V. B. Chipalkatti: We do not consider small differences in tensile strength, say less than *c.* 10 per cent, as technically significant.

Shri Upadhyay: You have given values of tensile strength throughout. Between tensile strength and tear strength which one do you consider more important from the point of view of end use? Even though you may have got an increase in tensile strength, it is possible that there is loss in tear strength.

Shri K. Manivannan: Tear strength is more important. We have determined this in one case, and the loss is *c.* 15 per cent.

Some Research Problems in Chemistry of Jute Cellulose*

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Indian Jute Mills Association Research Institute, Calcutta

Recent advances in the chemistry of jute cellulose have been reviewed with particular reference to individual constituents of the fibre, the mode of their association with one another, and their reactions with reagents commonly employed in jute processing and finishing. Reference has been made to the chemical aspects of bleaching, yellowing, softening, woollenizing and dyeing of jute fibres.

Cellulose occurs in close association with varying proportions of other cell wall constituents in plant materials and this led to the early belief that plant celluloses were either 'simple' or 'compound'. Simple celluloses were typified by cotton seed hair; compound celluloses contained, in addition to cellulose and hemicellulose, substances, such as lignin, pectin, etc., giving rise to what were called 'lignocellulose', 'pectocellulose' or 'mucocellulose'.

The frequent association of lignin with cellulose in plant and wood products, gave 'lignocellulose' special importance, and much work has been done on this group of compound cellulose. The isolation of the cellulosic fraction, however, created a major problem since this necessitated the removal of non-cellulosic substances. Various reagents and techniques have been developed with the primary object of removing non-cellulosic substances as completely as possible with minimum modification of the residual cellulosic aggregate.

Cross and Bevan, in 1895, devised a method for the isolation of cellulose from various fibres. Jute was considered to be typical of the lignocellulose group and also a convenient material for investigating the cellulose–lignin relationship in the cell wall. The method they employed for the isolation of cellulose[1] was: reaction of moist chlorine gas with the material previously treated with a dilute solution of sodium hydroxide at the boil and subsequent removal of the chlorinated products with boiling sodium sulphite. The product thus isolated, commonly known as 'Cross and Bevan cellulose', is an intimate mixture of cellulose and

* Paper read by Dr. A. B. Sen Gupta

other cell wall polysaccharides, namely, hemicelluloses, and does not represent pure cellulose.

In view of the marked loss of hemicellulosic components during the isolation of the cellulosic fraction by the Cross and Bevan method, Norman and Jenkins[2], in 1933. developed a more satisfactory method based on treatment with hypochlorite solution, instead of gaseous chlorine ; the sodium hydroxide pre-treatment, used by Cross and Bevan, was replaced by sodium sulphite, in order to avoid the loss of hemicellulosic substances. These workers also showed that the cellulosic fraction, isolated from various lignocellulosic substances, including jute, retains only a portion of the hemicellulosic material, predominantly xylan, while the rest is solubilized during the treatment. The fraction of hemicellulose which occurs in intimate association with cellulose was termed 'cellulosan' and the easily removable portion 'encrusting hemicellulose'.

Other investigators aiming at the isolation of the total polysaccharide fraction from lignocellulosic materials tried other methods for the preferential removal of lignin. Schmidt *et al.*[3] found that lignin can easily be removed by treating lignocellulosic material with aqueous chlorine dioxide, followed by extraction with hot alkaline sodium sulphite. Chowdhury and Majumdar[4] applied this procedure to jute fibre and observed that after-treatment with sulphite results in the removal of a portion of hemicellulose which can, however, be retained if the sulphite treatment is omitted and the material is washed with plain water. Sen Gupta and Callow[5], on the other hand, pointed out that the higher yield obtained by Chowdhury and Majumdar[4] is due to the incomplete removal of lignin degradation products and is not entirely due to the retention of the hemicellulosic fraction. These workers also showed that after-treatment with sodium sulphite was essential for the rtmoval of lignin degradation products, although it resulted in a simultaneous removal of an appreciable amount of hemicellulose. They further demonstrated that the maximum elimination of lignin degradation products with the minimum removal of carbohydrates can be effected by extracting the chlorine dioxide treated material with neutralized sodium sulphite solution. A higher yield of carbohydrate fraction from jute fibre can be obtained by the action of sodium chlorite under controlled conditions.

In 1942, Jayme[6] employed sodium chlorite as a delignifying agent for the isolation, from wood, of 'holocellulose', a term originally coined by Ritter and Kurth[7] to represent the total carbohydrate fraction present in plant materials. Chattopadhyay and Sarkar[8] were the first to employ this reagent under acidic condition on jute, and claimed to have isolated jute holocellulose containing only a trace of lignin. However, more recent work (not yet published) indicates that the jute holocellulose thus obtained is not only contaminated with an appreciable amount of lignin and its degradation products, but also suffers a distinct loss in the hemicellulosic

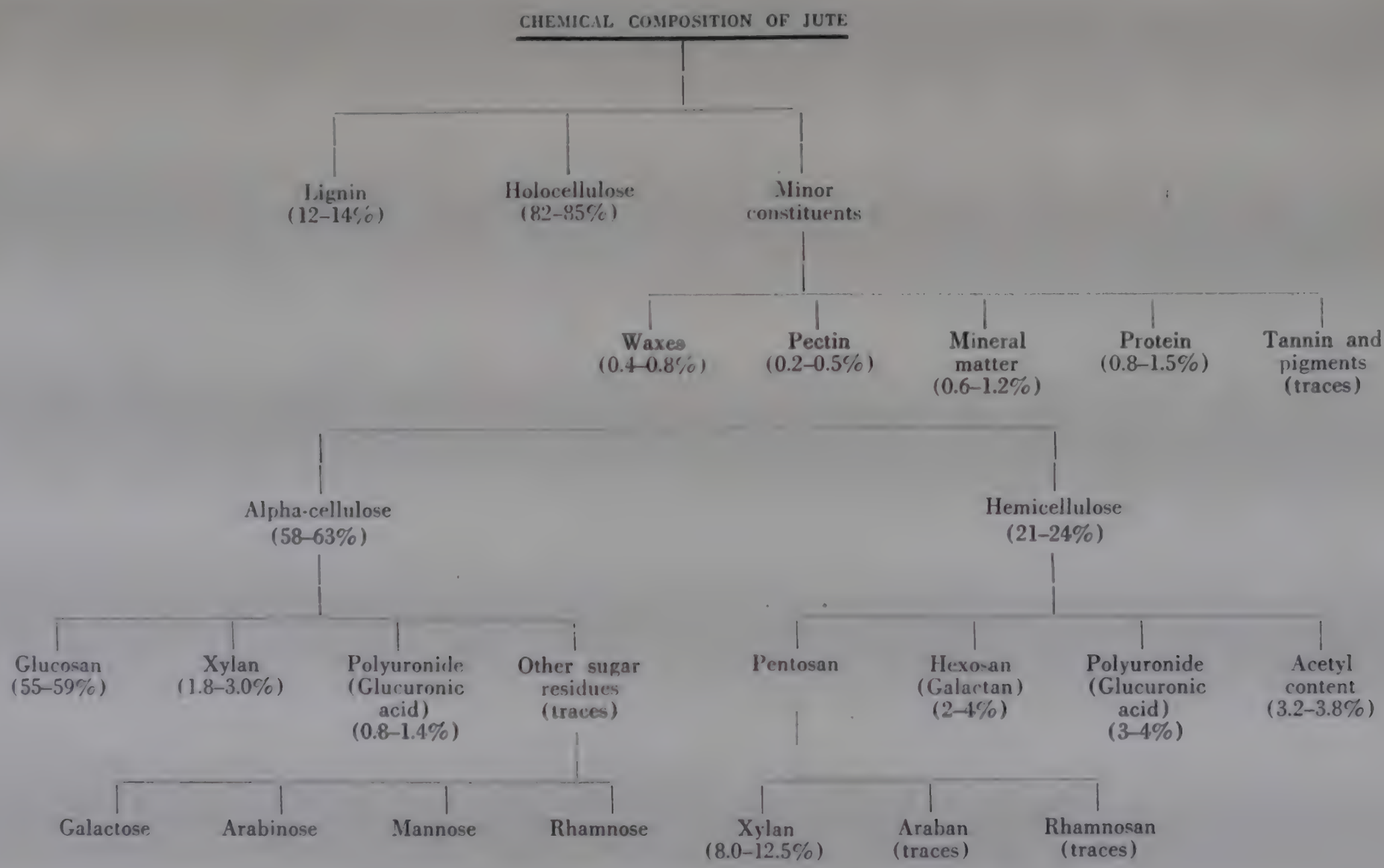
constituents and the apparent yield, although approaching the theoretical value of the total carbohydrate content of jute, is, in fact, a balanced product with positive and negative errors compensating each other.

The holocellulose when treated with 9–10 per cent or 17.5 per cent caustic soda yields alpha-cellulose which, until recently, was believed to be composed of glucose units with traces of xylose residues. Chromatographic analysis has, however, shown that jute alpha-cellulose is associated with a number of other sugar residues, besides xylose.

Although cellulose forms the skeletal structure of jute fibre, other non-cellulosic components, such as lignin and hemicellulose, are also of importance because of their effects on the physical, chemical and microbiological properties of the fibre. For example, almost complete removal of lignin or hemicellulose has a relatively small effect on dry yarn strength. The wet strength, however, is drastically reduced (by over 80%) if lignin alone is removed ; if hemicellulose alone is removed, the reduction in wet strength is roughly 50 per cent. When lignin and hemicellulose are removed together, even in small amounts, the dry strength is effected and begins to fall. Complete removal of either of these components tends to disintegrate the material and results in the production of small cellulose ultimates which are too short in length to spin and, consequently, of little value for textile purposes. These results have led Ridge *et al.*[9] to believe that jute fibre is basically composed of small units of cellulose (1.5–5 mm. in length) surrounded and cemented together by lignin and hemicellulose. Chemical treatment, therefore, depending on the extent of removal of lignin or hemicellulose affects the properties of the fibre.

More recently, investigations have been carried out for developing accurate methods for determining the non-cellulosic constituents of jute, especially xylan and lignin. In the conventional method, xylan is determined from the yield of furfural on distilling lignin-free material with hydrochloric acid. It has been shown by Macmillan *et al.*[10] that lignin does not interfere with xylan determination ; the hydroxy-methyl furfural which is generated from hexose residues under the conditions of furfural distillation, however, affects the results and for accurate determination of xylan, a correction factor has to be applied. The determination of lignin is made particularly complicated by its partial solubility in the acid employed for the hydrolysis of carbohydrate components, and the formation of furfural-lignin condensation products. Sen Gupta and Callow[11], however, have evolved a method involving the treatment of jute with 72 per cent sulphuric acid at 2°C.; the yield obtained corresponds approximately to the actual lignin content of the material.

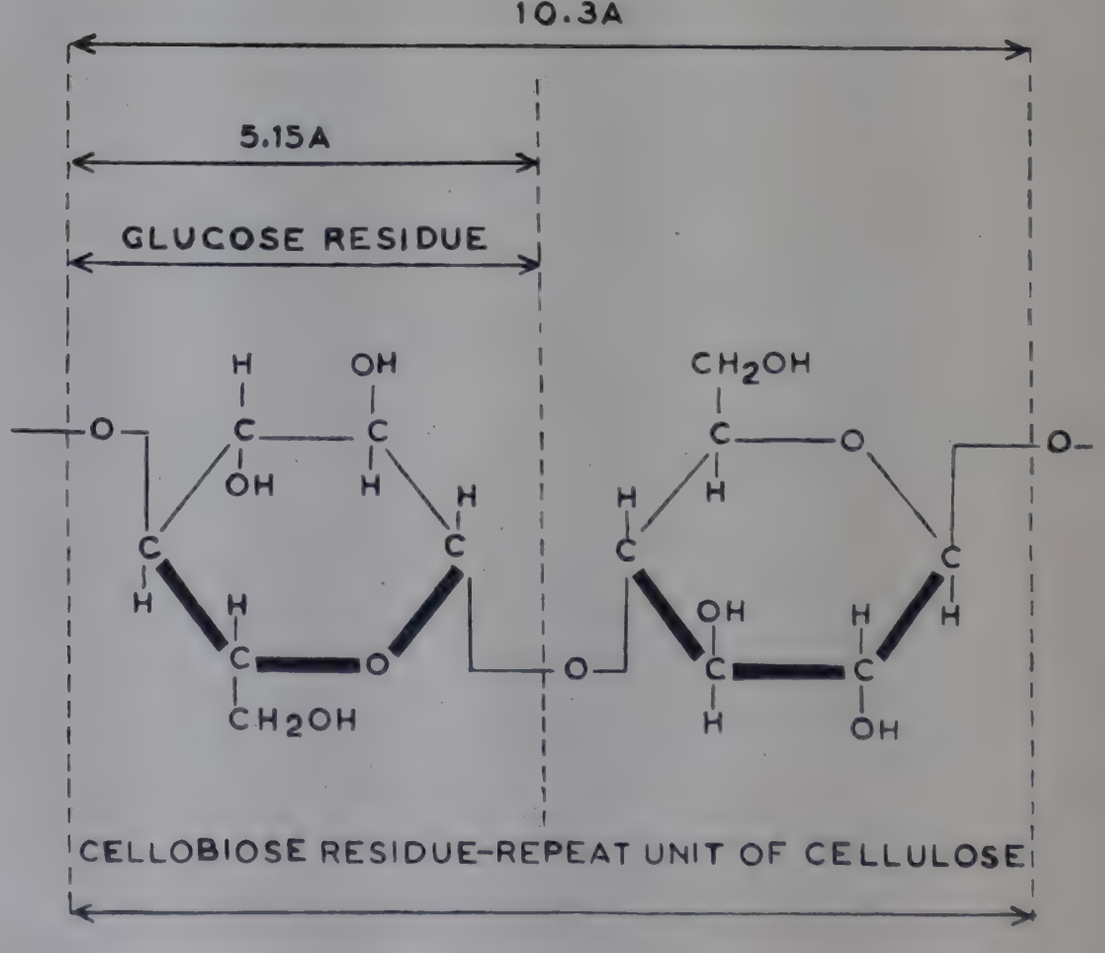
In brief, jute fibre is a complex mixture of chemical compounds which are built up by photosynthesis during the growth of the plant stem. According to our present knowledge, jute can be regarded as consisting


CHEMICAL COMPOSITION OF JUTE
Lignin (12–14%)
Holocellulose (82–85%)
Minor constituents
Waxes (0.4–0.8%)
Pectin (0.2–0.5%)
Mineral matter (0.6–1.2%)
Protein (0.8–1.5%)
Tannin and pigments (traces)
Alpha-cellulose (58–63%)
Hemicellulose (21–24%)
Glucosan (55–59%)
Xylan (1.8–3.0%)
Polyuronide (Glucuronic acid) (0.8–1.4%)
Other sugar residues (traces)
Pentosan
Hexosan (Galactan) (2–4%)
Polyuronide (Glucuronic acid) (3–4%)
Acetyl content (3.2–3.8%)
Galactose
Arabinose
Mannose
Rhamnose
Xylan (8.0–12.5%)
Araban (traces)
Rhamnosan (traces)

essentially of total polysaccharide or holocellulose (82–85%) and lignin (12–14%); the holocellulose being made up of true or alpha-cellulose (58–63%) and hemicellulose (21–24%). The hemicellulose fraction is a complicated mixture of pentosan (xylan 8–12.5%), hexosan (polyoses, 2–4%) and polyuronide (3–4%), along with acetyl groups (3.2–3.8%). Recent work, involving the use of paper chromatography, has shown that jute hemicellulose is composed of xylose, arabinose, rhamnose, galactose, mannose and methyl glucuronic acid, whereas jute alpha-cellulose is mainly glucose in association with small amounts of various sugar units, particularly xylose and mannose. It has been further shown that jute fibre is made up of chains of cellulose and hexosans, along with pentosans and polyuronides which may be either mixed or separate, the chains running more or less in the direction of the fibre axis. The stabilization of these chains is made possible by the presence of innumerable hydrogen bonds and different types of linkages.

The main structural unit of jute, as in plant materials generally, is cellulose which occurs in the form of a macromolecule consisting of a large number of beta-glucose anhydride residues condensed by means of 1–4 primary valency linkages through an oxygen bridge; the terminal carbinol groups alternate throughout the chain so that the repeating unit is cellobiose. A diagrammatic representation of the chemical composition of jute is given below.

Basic or fundamental knowledge on the chemistry of cellulose and the other constituents of jute can broadly be divided into three inter-



related categories, namely, (i) identification of the individual constituents ; (ii) mode of association of the constituents in the fibre ; (iii) reactivity of the constituents together with the reactions of jute fibre with reagents commonly employing in processing and finishing operations. Fundamental knowledge of this kind is, however, of little value until it can be applied to practical ends and a few applications are given below.

Bleaching

The non-cellulosic substances present in jute have a relatively high susceptibility towards oxidizing agents. Of the various oxidizing agents used in bleaching, alkaline hypochlorites are important. They are cheap and are readily available, and as such, they are commonly used for bleaching purposes. Improved results are, however, obtained by the use of alkaline hydrogen peroxide at elevated temperatures or by employing a combined treatment involving both alkaline hydrochlorite and hydrogen peroxide. The chemical reactions are mainly confined to the lignin component which is modified and slightly solubilized by the treatment. A reference has already been made to the effect of removing lignin and hemicellulose on dry and wet strengths of jute. Bleaching can also be effected by sodium chlorite activated with acid, and the improvement in colour brought about by this treatment is mainly dependent on the extent of lignin removed. Although the dry strength of jute is not altered to any great extent by the treatment, the wet strength is considerably reduced. A combination of sodium chlorite and hydrogen peroxide produces a good bleaching effect, but the wet tensile strength is decreased and this seriously limits its practical use.

Yellowing of jute

When jute material, particularly bleached jute material, is exposed to light, especially direct sunlight, for any length of time yellowing or browning takes place. This is a serious disadvantage in the utilization of bleached jute materials and in the subsequent dyeing of these materials. Recent research has shown that the yellowing or browning is due to the photochemical modification of the lignin component which results in the formation of quinonoid type compounds. The effect can be prevented by blocking the reactive hydroxyl groups of lignin by condensation reactions. The treatment necessary for preventing yellowing or browning is too expensive for practical adoption, and no method has as yet been devised to arrest or inhibit the photochemical degradation of jute fibre, which has been attributed to the formation of a volatile peroxide, possibly hydrogen peroxide. It is also worthy of note that yellowing or browning is not confined to jute, but is shown by other cellulosic substances containing lignin.

Softening and woollenizing

The inherent harshness and stiffness of jute fibre can be removed by treatment with dilute alkalies which remove a part of the hemicellulose

fraction and also break the alkali-sensitive cross linkages among the fibre components. The treatment softens the fibre and improves the feel ; further improvement may be brought about by additional finishing treatments. When cold concentrated caustic soda is used, the fibre undergoes a pronounced lateral swelling accompanied by shrinkage in length, in consequence of which a curly wool-like appearance is imparted ; this treatment is known as 'woollenizing' and the resultant material as 'woollenized jute'. The alkali-treated fibre is more extensible and its insulation property is improved due possibly to the interlocking of air in the fibre bundles. As a result of the treatment, there is a pronounced loss in strength, particularly in the wet state. The yellowish brown colour imparted as a result of the alkali treatment can be removed by bleaching. Woollenized jute can be blended with wool in varying proportions and used in the manufacture of carpets, blankets and low-cost clothing materials.

Dyeing

Jute materials, in the original or bleached states, can be dyed by the conventional dyeing operations but, in some cases, certain modifications in the dyeing techniques are necessary. The acidic nature of the fibre, due to the presence of carboxyl group in the polyuronic acid fraction, increases the affinity of basic dyestuffs and the increase of affinity can sometimes be so marked that it is necessary to retard the rate of dyeing in order to obtain evenness of shade.

Chemical modification

The chemical modifications brought about in the jute fibre during bleaching, softening and woollenizing have already been mentioned. Jute fibre also contains active groups which can be reacted with certain reagents to confer special properties. For example, if jute fibre is acetylated up to *c.* 16 per cent acetyl content under controlled conditions, the resulting fibre is fast to light ; the affinity for moisture absorption is decreased and the resistance to microbiological attack increased. Treatment with resin formulations, particularly of the melamine-formaldehyde type, result in the improvement of wet strength of bleached materials.

Microbiological aspects

The chemical components of jute are of importance in rot-resistance treatments. Jute alpha-cellulose is more resistant to fungal and bacterial attack than filter paper and less resistant than cotton cellulose. The hemicellulose in jute is more susceptible than cellulose to microbiological attack and have even been found to accelerate deterioration ; on the other hand, *c.* 25 per cent of the xylan in jute is as resistant to bacterial attack as alpha-cellulose. Lignin is resistant to attack by micro-organisms ; also it retards microbiological attack on the cellulose portion. Exposure to heat and light, and treatment with acid and alkali, renders jute more susceptible to fungal attack and more resistant to bacterial attack, while

the removal of vitamins and trace elements, helps to increase the resistance of jute to attack by fungi and bacteria.

Problems in the chemistry of jute and jute cellulose cover a very wide field. The commercial implications are also manifold, if it is borne in mind that about one million tons of jute goods are annually produced by Indian mills and this tonnage is obtained from the fibre portion of the jute plant which forms only 4–6 per cent of the green plant. Besides, there are other parts of the plant, such as jute stick (*c.* 65% of stem) and bast (35%) which can be commercially exploited. It is quite conceivable that if adequate attention is devoted to the utilization of jute plant for its chemical components as well as its fibre content, the value of this indigenous raw material for industry will be increased manifold.

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Discussion

Dr. Murthy: To what extent can woollenized jute be blended with wool?

Dr. A. B. Sen Gupta: The quantity of woollenized jute that can be profitably incorporated with wool depends largely on the type of union material to be manufactured from it. For coarse and cheap quality material like blanket, woollenized jute can easily be blended with wool up to 50 per cent.

Dr. V. B. Chipalkatti: What is the diameter of woollenized jute?

Dr. A. B. Sen Gupta: Owing to its multicellular nature, the microscopical structure of jute is very complicated compared with a unicellular substance like cotton. A single fibre of jute is, in fact, composed of numerous ultimate cells, the number in each bundle varying from 12–20. The diameter of a single jute fibre varies from 55–80 μ and after woollenizing treatment, the diameter of fibre is reduced to 25–50 μ, due partly to splitting of the bundle of cells and partly to the solubility of non-cellulosic constituents of jute in alkali.

Dr. V. B. Chipalkatti: I am interested in the tensile strength of the woollenized jute. How does it compare with that of wool?

Dr. A. B. Sen Gupta: The tensile strength of raw jute fibre usually varies from 4–5 g./denier and though after woollenization its strength is reduced to 3–4 g./denier,

yet its strength is considerably higher than that of wool, whose strength is of the order of 1.5–2.0 g./denier.

DR. H. WAKEHAM: What is the loss in wet strength on woollenizing ?

DR. A. B. SEN GUPTA: The wet strength of woollenized fibre gets reduced by *c.* 25 per cent compared with that of the untreated wet fibre.

DR. C. NANJUNDAYYA: What is the reason for the loss in wet strength?

DR. A. B. SEN GUPTA: Due to the removal of jute constituents and break-down of alkali sensitive linkages in jute, the strength of woollenized fibre is decreased and the enhanced loss on wetting is mainly due to the break-down of hydrogen bonds which were operative under dry state.

SHRI SHARMA: What is the extensibility of woollenized jute?

DR. A. B. SEN GUPTA: The extension at rupture of raw jute is 1–1.5 per cent while that of woollenized jute is of the order of 2.5–3 per cent.

SHRI L. R. SUD: What is the cost of woollenization of jute?

DR. A. B. SEN GUPTA: From laboratory experiments, it is rather difficult to state the actual cost of woollenizing precisely, but it appears that the cost of chemicals alone amounts to Rs. 20–25 per maund of jute treated.

SHRI SHARMA: Why do you mercerize jute under loose condition and not under tension?

DR. A. B. SEN GUPTA: No advantage would be obtained on mercerizing jute under tension, because even if the strength of fibre is somewhat increased, no woollenizing (formation of crimp or improvement in extension) is effected. Due to the solubility of non-cellulosic substances, the treatment under tension also fails to produce any improvement in lustre.

DR. C. NANJUNDAYYA: Is the crimp of woollenized jute permanent?

DR. A. B. SEN GUPTA: No. Most of the crimp (*c.* 75%) is lost on repeated stretching.

DR. C. NANJUNDAYYA: You say that yellowing of jute on exposure to sunlight is due to lignin. However, even with cotton, yellowing is observed after exposure to sunlight.

DR. A. B. SEN GUPTA: The extent of yellowing produced in jute is far more than that in cotton. The reasons for the formation of yellow colour in jute are entirely different from those in cotton. The latter turns slightly yellow on prolonged exposure and this is attributed to the formation of oxycellulose, while in jute some structural modification of lignin occurs leading to the formation of intense yellow colour within a comparatively short period. If the lignin content of jute is reduced to a very low level, say 0.2 per cent, then the material shows yellowing almost similar to that of cotton.

DR. C. NANJUNDAYYA: Has the natural oil content of the fibre any effect on yellowing?

DR. A. B. SEN GUPTA: Yes it has. The yellowing of jute is slightly decreased after removal of oil.

DR. P. K. CHOUDHURY: Does the D.P. of alpha-cellulose decrease on exposure ?

DR. A. B. SEN GUPTA: Yes it does. On exposing jute for *c.* 100 hr. in sunlight, the D.P. value of alpha-cellulose falls from 1,200–1,400 to 500–600.

DR. T. S. SUBRAMANIAN: How does lignin degrade cellulose ?

DR. A. B. SEN GUPTA: If jute and cotton are placed adjacent to each other and exposed to sunlight, the tensile strength of cotton which normally would have suffered a loss of *c.* 25 per cent in the absence of jute, is reduced by *c.* 45 per cent in the presence of jute. Jute under similar conditions of exposure, exhibits a much greater loss in strength of the order of 70 per cent. It has been found that a volatile peroxide, possibly hydrogen peroxide, is produced by lignin on exposure to sunlight and this

hydrogen peroxide is believed to degrade not only jute cellulose but also cotton when it is placed in proximity to jute, resulting in considerable reduction in strength.

SHRI T. S. A. PADMANABHAN: This is very similar to the result of exposure of cotton dyed with vat yellows or oranges. Here also if a dyed sample is placed together with an undyed sample, and both exposed to sunlight, the degradation of the undyed sample is considerably accelerated.

DR. A. B. SEN GUPTA: Yes, the reaction mechanism in both the cases is very similar and lignin acts almost as a dye during exposure to light.

DR. VIKRAM A. SARABHAI: Some thought should be given to the utilization of non-cellulosic impurities in jute.

DR. P. K. CHOUDHURY: Lignin is already being used in the plastic industry.

DR. A. B. SEN GUPTA: It appears preferable, however, to obtain lignin as a raw material for the plastic industry from waste products of the pulp and paper industry.

Isolation and Mode of Association of Jute Alpha-cellulose with other Sugar Residues

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The results of investigations, undertaken for developing a satisfactory method for the isolation of jute alpha-cellulose, and also ascertaining by chromatographic examination, the occurrence and mode of association of different sugar residues in jute alpha-cellulose, are given.

It has been found that a satisfactory yield of alpha-cellulose, with minimum xylan contamination, is obtained by treatment of delignified jute with 9.5 per cent caustic soda at room temperature.

By employing sulphuric acid (1 *N*) for the hydrolysis of alpha-cellulose, and the technique of interrupted development of chromatogram, it has been found that, in addition to glucose, xylose and arabinose previously reported, uronic acid, galactose, mannose and rhamnose are also present in association with jute alpha-cellulose. The investigation points to the probable presence of xylose and mannose residues as integral parts of alpha-cellulose in the crystalline region and of other sugar residues in the amorphous region.

Although cellulose constitutes the main structural basis of vegetable fibres, it does not occur in a relatively pure state, except in cotton seed hairs. In plant materials generally, and particularly in lignocellulosic substances, cellulose occurs in close association with high percentages of non-cellulosic cell wall constituents, especially lignin and hemicellulose.

The isolation of cellulose from a plant substance is complicated due to the fact that the removal of hemicellulose can be effectively carried out only if the material is previously delignified. In the standard method of treatment, recommended by the American Chemical Society (A.C.S.), the delignified material is reacted with 17.5 per cent caustic soda solution when the hemicellulosic components are solubilized, leaving an insoluble residue which is termed alpha-cellulose, in order to differentiate it from the pure cellulose obtained from cotton seed hairs.

Extensive studies on wood alpha-cellulose have revealed that the material is associated with varying amounts of mannose and xylose. In the case of jute, however, Norman[1] is of the opinion that alpha-cellulose exists in intimate association with xylan, which is stated to occur with glucose in the form of mixed or homogeneous chains. Sarkar *et al.*[2] on the other hand, are of the view that no chemical linkage is involved between

TABLE 1—YIELD AND XYLAN CONTENT OF JUTE ALPHA-CELLULOSE ISOLATED BY DIFFERENT METHODS

Method	Yield %	Xylan content %
One treatment with 17.5% alkali (A.C.S. method)	65.6	5.64
Two treatments with 17.5% alkali (A.C.S. method)	63.2	3.10
One treatment with 17.5% alkali, residue washed as suggested by Sarkar *et al.*[2]	65.7	5.56
One treatment with 9.3% alkali	62.0	1.95
Two treatments with 9.3% alkali as suggested by Sarkar *et al.*[2]	62.6	1.87
Three treatments with 9.3% alkali	62.1	1.99

xylan and cellulose, and alpha-cellulose, entirely free from xylan, can be prepared from jute, provided a modification is introduced in the isolation procedure. The modification suggested consists in either altering the method of washing the alkali-insoluble residue obtained by the standard procedure, or applying two successive treatments of 9.3 per cent alkali, instead of one treatment with 17.5 per cent alkali. Das *et al.*[3] on the other hand, contend that jute alpha-cellulose is invariably associated with a certain amount of xylose and arabinose irrespective of the method of isolation and, in addition, the pentose sugars exist in chemical combination with the cellulose molecule. More recently, it has been shown by Adams and Bishop[4] that both xylose and arabinose occur in jute alpha-cellulose, but these workers have failed to detect any oligosaccharide containing glucose, xylose and arabinose, as claimed by Das *et al.*

It is evident from the above brief review that conflicting views still prevail with regard to the association of jute alpha-cellulose with different sugar residues. The work described here was undertaken with the object of developing a standard method for the isolation of alpha-cellulose and ascertaining by chromatographic examination, the occurrence and mode of association of sugar residues in jute alpha-cellulose.

Isolation of alpha-cellulose

Effect of method of isolation on yield of xylan in alpha-cellulose—Jute fibre after preliminary purification, was delignified by hot acidic sodium chlorite and the residue (holocellulose) was treated with caustic soda under varying conditions for the isolation of alpha-cellulose. The resulting material was analysed for xylan content by the standard furfural method as modified by Macmillan *et al.*[5] The results are summarized in Table 1.

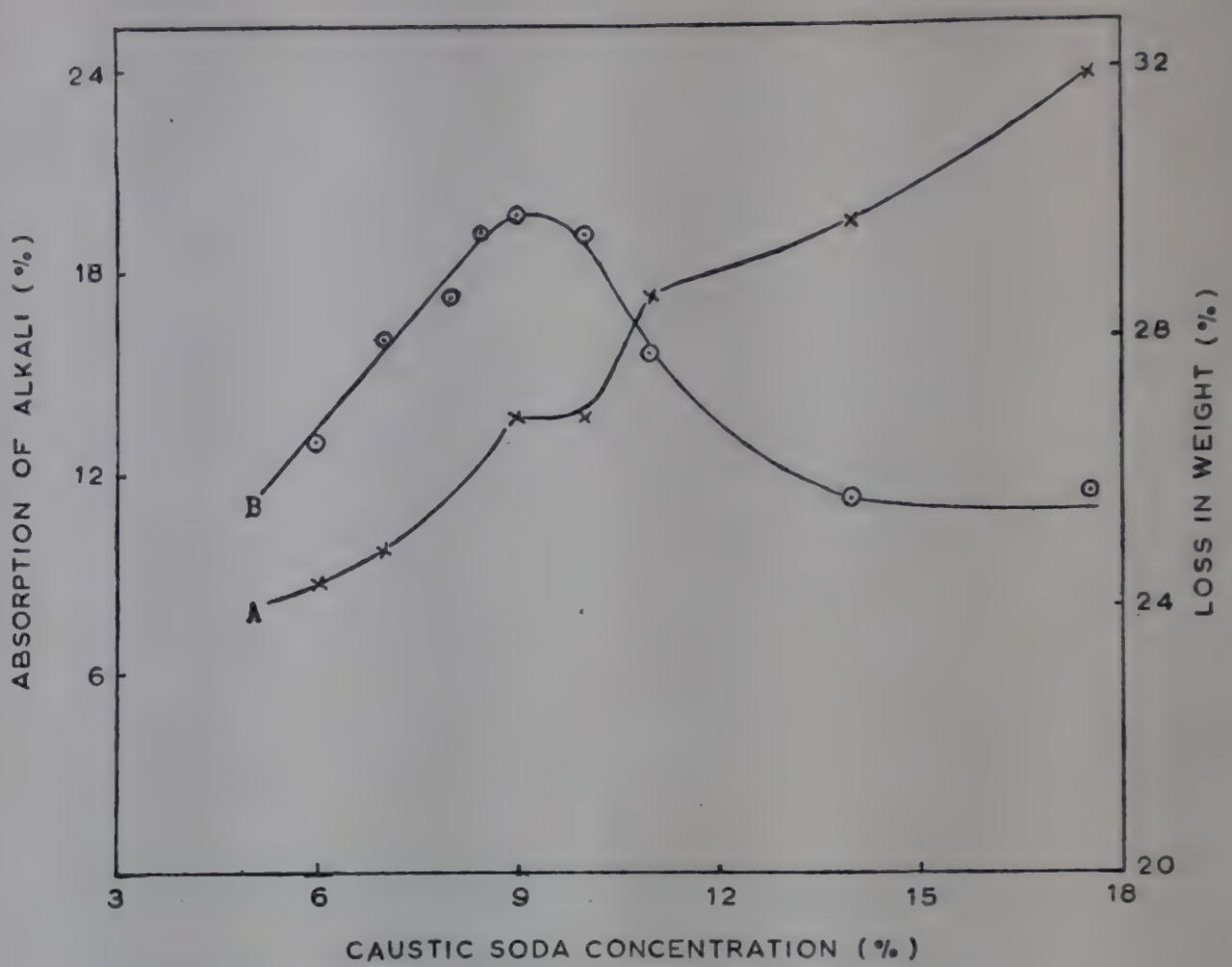

FIG. 1—EFFECT OF CAUSTIC SODA CONCN. ON ALKALI ABSORPTION AND LOSS IN WT. OF HOLOCELLULOSE—A, ALKALI ABSORPTION; B, LOSS IN WT.

It is evident from Table 1 that jute alpha-cellulose is associated with a measurable amount of xylan irrespective of the method of its isolation. Two successive treatments with 17.5 per cent caustic soda lowers both the yield, and xylan content of alpha-cellulose. The yield of alpha-cellulose and its xylan content are unaffected by the number of treatments with 9.3 per cent alkali. A single treatment at this lower concentration of alkali is more effective for the removal of xylan than two treatments at 17.5 per cent.

Effect of caustic soda on jute holocellulose—Since none of the alkali treatments examined so far was capable of eliminating xylan from alpha-cellulose, the action of different concentrations of caustic soda was next investigated. The effect of varying the alkali concentration (room temperature ; duration of treatment, 1 hr.) on alkali absorption and loss in weight of holocellulose is shown in Fig. 1. It will be seen that there is a distinct inflection in the absorption at 9–10 per cent alkali concentration. As in the case of cotton, this inflection is likely to correspond with the optimum condition for the swelling of holocellulose, as a result of which the material has suffered the highest loss in weight, and consequently gives the lowest yield of alpha-cellulose.

It is well known that a decrease in the reaction temperature brings about a considerably greater swelling of cotton cellulose in alkali, and the

TABLE 2—EFFECT OF VARYING ALKALI TEMPERATURE ON YIELD, XYLAN CONTENT AND D.P. OF ALPHA-CELLULOSE

Temperature °C.	Yield %	Xylan content %	D. P.*
–7	63.8	5.42	1053
4	65.1	5.84	1079
20	63.4	4.00	1079
28	62.1	1.97	1085
50	61.2	..	..
100	56.2	2.01	1010

* As determined by the cuprammonium viscometric method

investigation was extended to the study of the effect of varying the temperature on the yield of alpha-cellulose, the concentration of caustic soda being kept constant at 9.5 per cent. The xylan content and the degree of polymerization (D.P.) of the product were determined to ascertain whether any degradation has taken place. The results obtained are given in Table 2.

None of the samples of alpha-cellulose is free from xylan (Table 2). Although the cellulose has undergone a higher degree of swelling at lower temperatures, particularly at 7°C. or 4°C. when the material is completely dispersed in alkali, the xylan content is appreciably higher than that of samples treated at higher temperatures. The results indicate that the lowering of xylan content at higher temperatures is accompanied by a reduction in the yield of alpha-cellulose. Approximately 2 per cent of xylan appears to be intimately associated with cellulose and even drastic treatment which appreciably affects and degrades cellulose, fails to remove that xylan. The degraded cellulose is, however, solubilized in alkali and the D.P. of the isolated material remains practically unaffected. It will be clear from Table 2 that alpha-cellulose with minimum contamination of xylan is obtained in a satisfactory yield by the treatment of cellulose with 9.5 per cent alkali at room temperature.

Chromatographic analysis

In the chromatographic examination of cellulosic substances containing other sugar residues, the usual procedure of complete hydrolysis with 72 per cent sulphuric acid is likely to give erroneous results due to, interference by glucose which is present in relatively large amounts. In the course of our study on jute alpha-cellulose, it was observed that by following the usual procedure, only glucose and xylose are detected. By using dilute sulphuric acid solution, instead of concentrated acid, only partial hydrolysis is effected and the conversion of glucosan into glucose is greatly restricted; and by using the technique of interrupted development of

chromatogram, it is possible to identify a number of sugars in addition to those already reported.

Jute alpha-cellulose (10 g.) was partially hydrolysed by heating with N sulphuric acid for 1 hr. when the material suffered 4–6 per cent loss in weight (extent of loss depending upon the method of isolation). The extract was hydrolysed by refluxing for 6 hr., neutralized with barium carbonate to *p*H 5–6, concentrated at 35°C. to a small bulk, and chromatographed on Whatman No. 1 filter paper with *n*-butanol-acetic acid-water (1 : 0.24 : 1) as solvent ; sugars were detected by spraying with aniline hydrogen phthalate. When the chromatogram was run at a stretch for 97–120 hr. in order to separate individual components, the spots of sugars occurring in minor quantities became too faint for detection by visual examination. On interrupting the flow of chromatogram and subjecting the paper to three successive runs, for 56, 36 and 30 hr. respectively, sugars could be identified, although the shape of the spots was different from that obtained after a single run. A typical chromatogram (Fig. 2) of the hydrolysate of alpha-cellulose (prepared by two different methods, namely, the A.C.S. and the 9.5 per cent alkali treatment) shows that presence of barium uronate, galactose, mannose and rhamnose, in addition to glucose, xylose and arabinose already identified. Individual sugars were isolated after separation on Whatman No. 3 mm. filter paper and confirmed by Rf values and chemical tests whenever possible.

In an attempt to elucidate the possible mode of association of different sugar residues detected in jute alpha-cellulose, the material was heated with N/2 sulphuric acid for 1 hr. and the product of incomplete hydrolysis was chromatographed as usual when 10 different spots, pink and yellow in colour, developed on spraying with aniline hydrogen phthalate (Fig. 3). The substances corresponding to spots No. 1, 6, 8 and 10 were isolated after separation on Whatman No. 3 mm. filter paper, the former two spots being yellow and the latter two pink in colour. The extracts obtained from the individual oligosaccharides were completely hydrolysed by prolonged boiling with acid, then chromatographed as described before, and the component sugar residues identified. Although oligosaccharides of spots No. 1 and 8 gave different colours and are of widely different Rf values, both are found to consist of galactose, glucose, xylose and traces of mannose. The oligosaccharide of spot No. 6 is found to comprise galactose, glucose and xylose while that of No. 10 is composed of glucose and xylose possibly with traces of mannose. It appears highly probable, therefore, that mixed chains of sugar components, identified in individual oligosaccharides, occur in jute alpha-celulose.

Alpha-cellulose prepared by 9.5 per cent alkali treatment to three successive extractions with N sulphuric acid (the original material suffered a total loss of *c.* 13% in weight) was found to contain glucose, xylose and mannose ; the second and third extracts also contain glucose, xylose

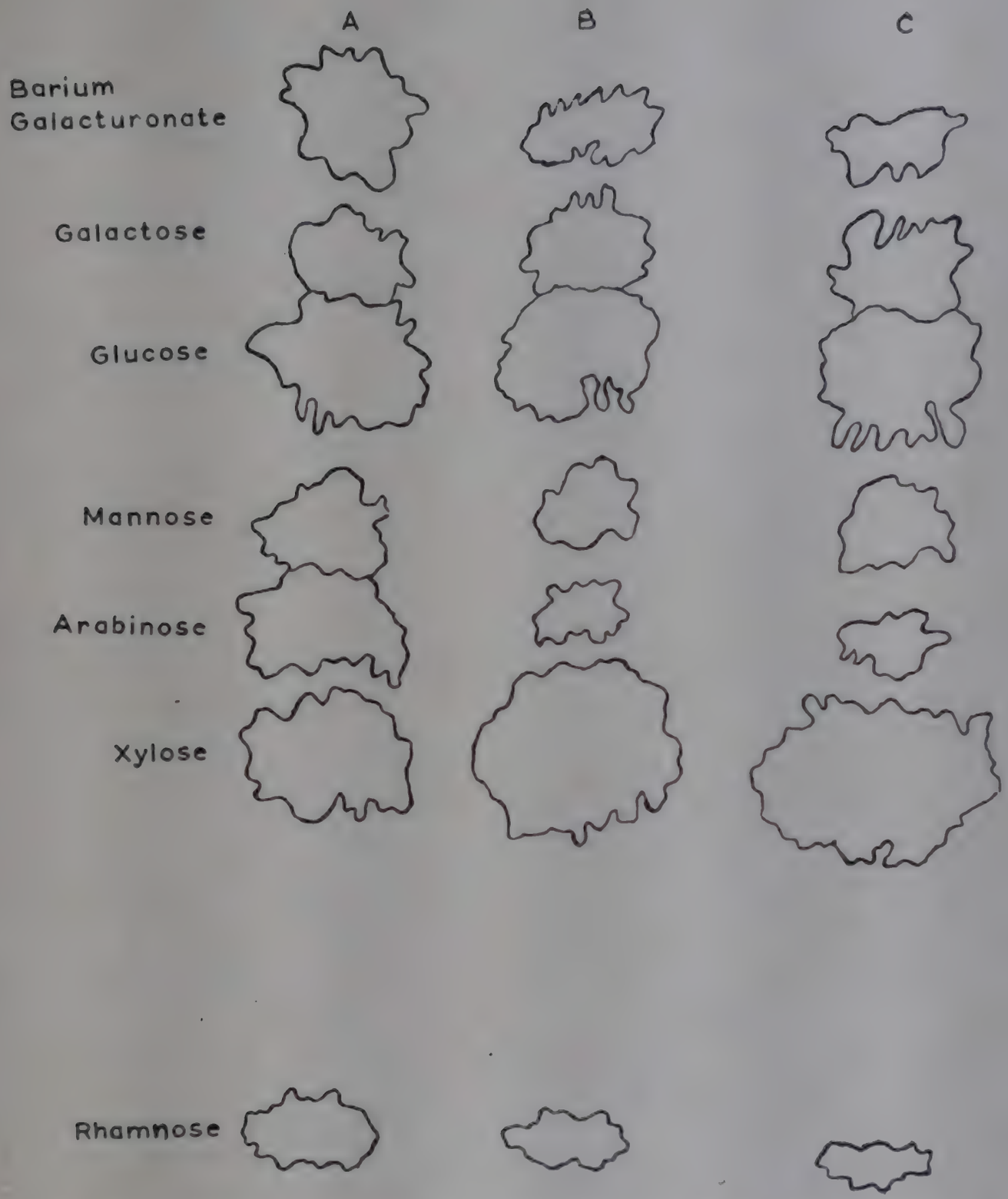

FIG. 2—CHROMATOGRAM WITH 3 SUCCESSIVE RUNS OF 30, 36 AND 56 HR.—A, REFERENCE SUGARS; B, ALPHA-CELLULOSE ISOLATED BY TREATMENT WITH 9.5% ALKALI; C, ALPHA-CELLULOSE ISOLATED BY TREATMENT WITH 17.5% ALKALI

and mannose. Obviously, therefore, the additional sugar residues found in the first extract are present in the amorphous region, while xylose and mannose appear to occur in the crystalline region. The acid-insoluble cellulosic residue was fractionated by dissolving in cuprammonium solution, and addition of acetone, and then hydrochloric acid. The first fraction constituting 73 per cent, and apparently of larger chain length, was composed of glucose, xylose and mannose. The fraction obtained by acidification, representing 25.5 per cent, contained predominantly glucose

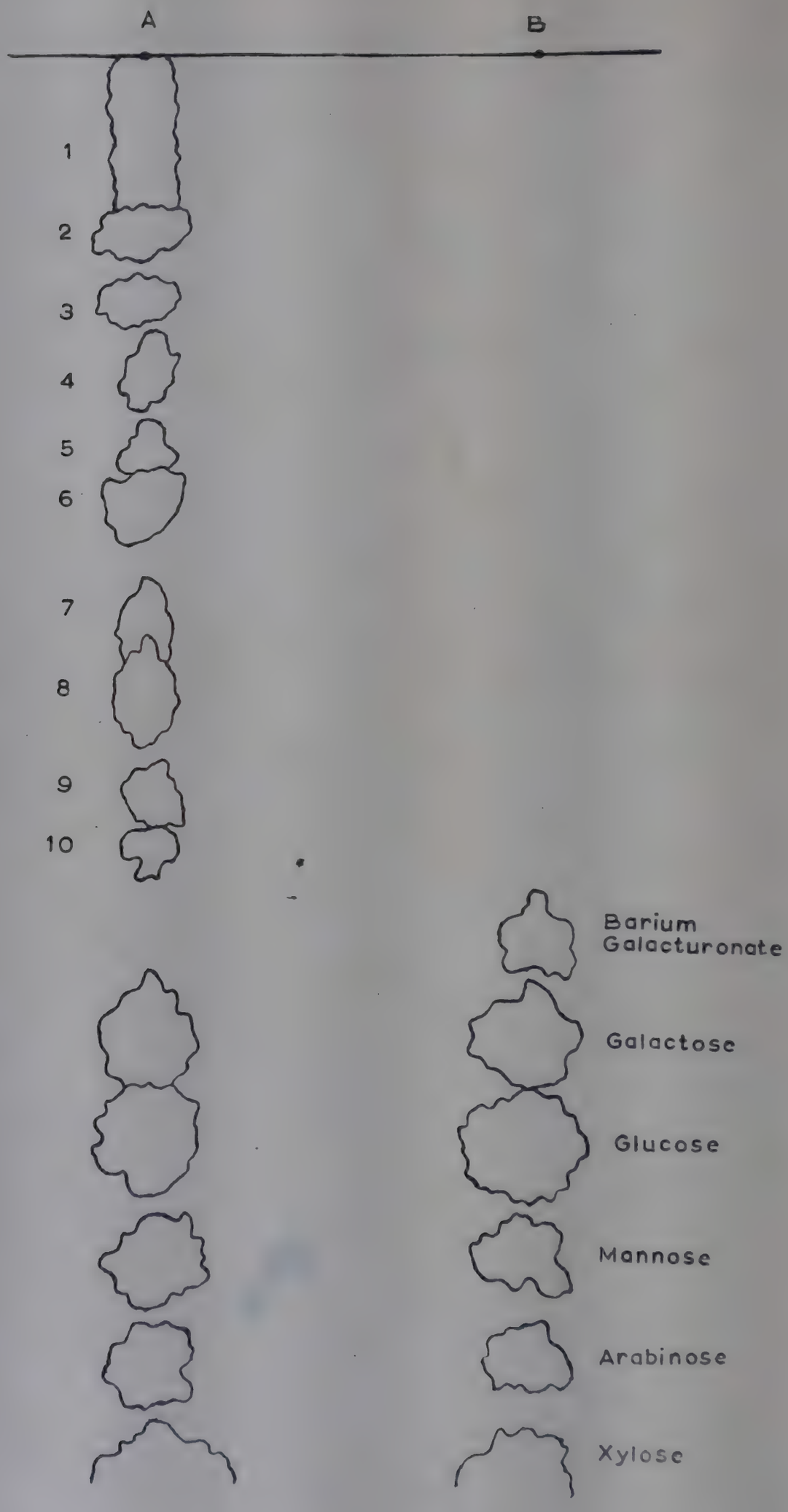

FIG. 3—CHROMATOGRAM OF ALPHA-CELLULOSE PARTIALLY HYDROLYSED WITH N/2 SULPHURIC ACID—A, PARTIALLY HYDROLYSED ALPHA-CELLULOSE; B, REFERENCE SUGARS

with only a trace of mannose. Xylose and mannose residues, therefore, seem to be integral parts of alpha-cellulose, occurring in the crystalline region and it is highly probable they exist in chemical combination with the cellulose chain.

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Discussion

Dr. P. K. Choudhury: How do you determine hydroxy-methyl furfural ?

Dr. A. B. Sen Gupta: On subjecting the distillate obtained with hydrochloric acid to redistillation, hydroxy-methyl furfural is quantitatively destroyed along with a small portion of true furfural. On determining the loss of true furfural from a separate experiment, the content of hydroxy-methyl furfural is calculated.

Dr. C. Nanjundayya: Why have you employed the cuprammonium viscosity method for determining D.P. values when the more accurate method of cupriethylenediamine is available?

Dr. A. B. Sen Gupta: As we are interested only in a comparative (not absolute) value of D.P., any standard method seems to be equally suitable. So far as I know, the cuprammonium method is extensively employed in the U.K. and in Europe, while cupriethylenediamine method is used in the U.S.A.

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